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AUTHOR: _____Peter A. Lurker_____

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ORGANIZATION   LOCATION

STATEMENT(s):

ATMOSPHERIC RELEASE OF ORGANIC CHLORINATED COMPOUNDS FROM

THE ACTIVATED-SLUDGE WASTEWATER TREATMENT PROCESS

A dissertation submitted to the

Division of Graduate Studies
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

in the Department of Environmental Health
of the College of Medicine

1980

by

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ABSTRACT

The objective of this study was to investigate some of the potentially controlling factors influencing the atmospheric release of volatile organic compounds from the activated-sludge sewage treatment process. The study consisted of field studies at an activated-sludge treatment plant and laboratory studies with a bench-scale aeration vessel. The field studies were designed to evaluate the wastewater and airborne concentrations of three chlorinated compounds: hexachlorobicycloheptadiene (Hex-BCH), heptachlorobicycloheptene (Hex-VCL) and chlordene at various locations of the plant. The laboratory aeration unit was used to investigate the influence of aeration rate, suspended solids concentration, and detergent level on the rate of stripping of Hex-BCH and chloroform from a simulated wastewater solution. ——>

Bench-scale aeration experiments were conducted with a simulated wastewater solution to assure a uniform comparison of the results for the various test parameters. The wastewater solution consisted of biologically-digested, vacuum-filtered waste activated-sludge from a local treatment plant. The sludge was further vacuum and heat dried in the laboratory, sifted through a Tyler 30 mesh screen and homogenized in a small amount of double distilled water (DDW). Detergent, a standard linear alkylate sulfonate (LAS), Hex-BCH, and chloroform were combined with the sludge in two liters of DDW. The wastewater solution was aerated and aliquots were withdrawn after 0.25, 0.5, 1, 2, 3, 4, 5 and 6 hours of aeration. Five aeration rates (17.5, 35, 70, 180, 280

cc/min.), three suspended solids concentrations (500, 1000, 1500 mg/L) and three detergent levels (0, 20, 40 ppm) were used. All possible combinations were investigated (5 x 3 x 3) and each of the 45 experiments was performed in duplicate.

Sample preparation consisted of saturating 5 mL aliquots with sodium chloride and extracting with an equal amount of petroleum ether (PE). The air samples, collected on Chromosorb 102, were desorbed with 2 mL PE. Analysis was accomplished by gas chromatography with electron capture detector (GC/ECD).

The field study revealed that the highest wastewater concentrations of the test compounds (Hex-BCH, Hex-VCL and chlordene) were found in the sludge of the aeration basins, which suggest significant adsorption of the test compounds to the solids. Comparison of the airborne concentrations of the different aeration basin types at the plant: contact, stabilization and digestion, suggested higher release from the contact and stabilization basins than the digestion basins. The higher air flow through the contact and stabilization basins is considered to be the primary factor partially responsible for this. In addition, the digestion and stabilization basins have much higher suspended solids levels than the contact basins, which may suppress the aerial stripping. Emission rate studies indicate that approximately 35% of the Hex-BCH received in the plant influent was dispersed to the atmosphere from the contact aeration basins and only 0.2% from the grit-chamber weir. The plant effluent wastewater concentrations of these substances were

reduced at least 80% below influent levels because of airborne release and suspended solids separation in the clarifiers.

In the bench-scale aeration unit study, first order kinetic decay behavior was found for the stripping of Hex-BCH and chloroform. The influence of aeration rate, suspended solids concentration and detergent level was statistically significant for the release of Hex-BCH. The increase in aeration rate appreciably improved the release of Hex-BCH while increasing the level of suspended solids inhibited aerial stripping. A linear relationship was found between detergent level and stripping rate. Aeration rate was the only significant parameter influencing the aerial release of chloroform. The results suggest that Hex-BCH is stripped from an adsorbed state whereas chloroform is stripped from a dissolved state.

The demonstrated release of a hazardous organic compound into the ambient air at the treatment plant suggests that more attention should be given to air stripping of other potentially toxic compounds.

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1.0 INTRODUCTION

1.1 Statement of Problem

The objective of this research was to investigate some of the potentially controlling factors influencing the atmospheric release of organic compounds from the activated-sludge sewage treatment process. Field studies were used to ascertain the various locations at an activated-sludge sewage treatment plant where atmospheric release of representative chlorinated compounds occur. Laboratory studies assessed the influence of aeration rate, surfactant and suspended solids concentration on the atmospheric release of two representative chlorinated compounds from an aerated vessel containing a simulated wastewater sludge solution.

Sewage treatment plants can receive toxic or hazardous material by direct discharge from industrial facilities or by illegal dumping into the sewer system. Despite enforcement of regulations, undesirable dis- charges will likely continue for some time into the future. Volatile compounds can be released to the atmosphere from the wastewater during treatment. Release can occur at a number of locations in the plant including the wet well, grit chamber, aeration basins and settling tanks. Release at the grit chamber is enhanced by flow over a weir and by aeration. Of particular concern, is the potential of long-term release in the activated-sludge unit. The process contains biomass which can adsorb many volatile compounds and initially depress the atmospheric release. After the biomass is recycled from the settling tank, the aeration process in the aeration basin can again

strip volatile compounds. This recycling and stripping process can continue long after the actual passage of the contaminant slug flow through the treatment plant. Thus, it can not be assumed that the exposure of sewage treatment workers is limited to the time of the actual passage of a slug flow through the treatment plant. Because of the large surface area, the aeration process and the recycling feature of the process, the activated-sludge process can be an extensive source of volatile compound release to the atmosphere in the sewage treatment plant and warranted evaluation.

The specific aims of this research were:

1. To test the hypothesis that the receipt of chlorinated volatile compounds in the influent of an activated-sludge sewage treatment process will result in atmospheric release of the compounds at various locations in the plant.

2. To validate a mass balance technique to estimate the emission rate of a volatile compound from the contact aeration basin and grit-chamber weir. Air sampling measurements were incorporated into atmospheric dispersion models to yield calculated emission rates to allow a comparison with the estimated emission rates derived from the mass balances.

3. To develop a laboratory bench-scale treatment unit and method which is capable of measuring the atmospheric release of volatile compounds from the aeration vessel.

4. Investigate the effects of aeration rate, suspended solids concentration and surfactant concentration on the atmospheric release

of two representative chlorinated compounds from a bench-scale laboratory unit.

5. Based on the laboratory data, suggest operating procedures to minimize the exposure of the sewage-treatment workers to the airborne organic compounds.

1.2 Background

1.2.1 Brief Description of the Activated-Sludge Process

In the activated-sludge process as depicted in Figure 1, microorganisms, principally bacteria, use organic carbon as an energy source. Oxygen and nutrients are required by the bacteria to convert the organics to CO_2, H_2O and new cell mass, as follows:

$$\text{organics} + O_2 \xrightarrow[\text{bacteria}]{\text{nutrients}} \text{new cell mass} + CO_2 + H_2O$$
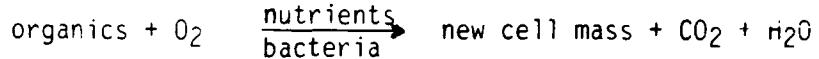
Aeration is provided to assure sufficient oxygen and mixing. The activated sludge consists of flocculent masses of microorganisms and non-living organic and inorganic matter. Colloidal and suspended material is adsorbed on the sludge to provide nutrients for new cell mass production. After a period of about 1-3 hours, this mixed liquor effluent is allowed to settle in a clarifier and a major portion of the settled sludge is returned to the aeration tank and mixed with the raw sewage to maintain a desired biomass level. The supernatant from the clarifier will frequently flow to a chlorine contact basin, not shown on Figure 1, and then be released to receiving waters as the final effluent from the treatment plant.

1.2.2 Previous Investigations of Release of Volatile Organic Compound
from Wastewater Systems

Engelbrecht et al. (1) investigated petrochemical wastes in dis-
tilled water and noted first order stripping of butanone and acetone
during aeration. The data empirically fit a first order decay model:

$$Ka = CQ^N \qquad \text{Eq. (1)}$$

where   Ka = first order decay constant

   C = constant

   Q = aeration rate

   N = empirical exponent

C was depended on the specific compound while N was a function of the
geometric aspects of the aeration vessel. Grady et al. (2) reported
that this first order decay constant was depended on the tank geometry
and that at higher temperatures (40°C) propionaldehyde did not follow
first order decay. The developed empirical expressions for the decay
constant in terms of the aeration rate were strongly depended on the
specific set of experimental conditions. When a filter paper pulp was
incorporated to simulate a biomass, the suspended solids had no effects
on the decay constant (2). However, this constant was determined from
concentrations of volatile organic compounds in the supernatant
following centrifugation of the aeration vessel liquor aliquot. This
experimental approach only measured the concentration of the dissolved
component in the centrifuged supernatant. No information was reported
on the concentration of the adsorbed component on the filter paper
pulp.

Goswami (3) studied the stripping of volatile organic compounds such as propionaldehyde, valeraldehyde, butyraldehyde, acetone and methyl ethyl ketone (MEK) from a bench-scale activated-sludge treatment unit. He noted that autoxidation of a volatile compound can occur as the compound contacted the oxygen within the rising air bubbles. Also he observed that when the air stripping was the sole mechanism of removal, that is no biological degradation or autoxidation takes place, the stripping decay constant can be used to predict the steady-state concentration of the test compound in a continuous flow reactor. However, the same aeration rate and aeration liquor volume must be maintained in both the batch and continuous flow operations. The stripping of acetone and MEK followed first order kinetic decay. The aldehydes did not conform to this first order decay behavior over the entire course of removal, probably because of autoxidation.

Thibodeaux and Millican (4) developed an experimental desorption device to quantify the relative volatilization rates of organic matter in industrial wastewaters. By using this experimental unit the maximum quantity of organic material in wastewater than can be volatilized into the atmosphere can be determined. They noted that the volatile material desorbs readily during sewage operations employing aeration. In addition, significant amounts also desorb under natural environmental conditions as water flows in open channels or undergoes treatment in large surface lagoons or basins. Seventy-five industrial wastewater samples representing 26 industry types were tested in this desorption apparatus. Sixty-four (85%) contained

detectable air-strippable fractions. Thibodeaux and Millican concluded that the quantity of volatile material in industrial wastewater is significantly higher than expected. This work is of limited value since field studies are necessary to validate whether the maximum release of volatile compounds occurs.

Tischler et al. (5) developed a laboratory-scale activated-sludge unit which allowed a complete carbon balance of both the liquid and gaseous influents and effluents. This laboratory unit allowed study of acclimated biomass during its activated-sludge treatment. The volatile hydrocarbon emissions in the off-gas from this laboratory unit were measured with a total hydrocarbon analyzer. Results with two industrial petrochemical wastewater samples demonstrated that biological removal of the hydrocarbon was far more significant than removal by air stripping of the volatile components. Only 0.22 and 0.31 percent of the total organic carbon (TOC) of the petrochemical waste was released to atmosphere. Even more impressive results were shown by a study of a wastewater sample from a regional wastewater treatment plant; of a potential stippable component of 20 percent of raw wastewater TOC, only 0.04 percent was stripped.

A compendium of air stripping of organic compounds from industrial wastewater was prepared by Thibodeaux (6). The thermodynamic basis for desorption was presented as well as the comparison of desorption from a packed column was made to the desorption of volatile compounds from dilute aqueous solutions present in the activated-sludge process. This packed column apparatus was previously discussed above from the

paper by Thibodeaux and Millican (4). A detailed discussion was presented on the modeling of combined biochemical oxidation and air-stripping of volatile compounds. The model incorporated the volatility of the organic compounds, the biological removal rate due to the active biomass and the physical characteristics of the aeration basins. The calculated total organic carbon (TOC) removal by air-stripping ranged from a high of eleven percent of the total TOC removal for acetaldehyde, to a low of 0.012 percent of the total TOC removal for phenol at a biomass concentration of 3,000 mg BOD/L. The paper pointed out that air sampling of operational field activated-sludge units was the only accurate means to assess the magnitude of desorption of the organic compounds from the wastewater.

The studies of Goswami (3), Tischler et al. (5) and Thibodeaux (6) did not include testing of volatile compounds with unacclimated biomass. Significant atmospheric release may occur until the biomass adapted to any new volatile component. In an activated-sludge treatment plant, infrequent slug flows of a volatile component may contact the unacclimated biomass and instead of being consumed, be released to atmosphere.

1.2.3 Mechanisms of Volatile Compound Release

Following receipt of a volatile compound in the wastewater influent of an activated-sludge treatment plant, the compound undergoes a complex distribution throughout the plant. The compound can remain in the wastewater liquid phase, where it is either dissolved in the

aqueous phase and/or any other liquid phase (i.e., oil) or adsorbed
onto any suspended solids. The compound can transfer from these liquid/
solid phases to the atmosphere (gas phase). This study was primarily
concerned with the atmospheric releases of volatile components.
Several mechanisms facilitate this transfer from the liquid/solid
phases to atmosphere, which include: evaporation from liquid surface,
air stripping, and droplet formation.

1.2.3.1 Evaporation from Liquid Surfaces

Evaporation from the liquid surface will release a volatile com-
pound to atmosphere. MacKay and Wolkoff (7) developed a half-life
expression for a contaminant in water based on evaporation loss, which
is as follows:

$$T = \frac{12.48 \, G P_w C_{is}}{10^6 \, E \, P_{is} M_i} \qquad \text{Eq. (2)}$$

where T = half-life of the contaminant (days).

G = the weight of water in the system (grams).

P_w = partial pressure of water (24 mm Hg).

C_{is}= solubility of the solute in water (mg/L).

E = weight of water evaporated per day (g/m^2/day).

P_{is}= vapor pressure of pure solute (mm Hg).

M_i = molecular weight of the solute (g/gmole).

Assumptions for this expression include:

    i. Contaminant concentration is truly in solution and not sus-
pended, colloidal, ionic, complexed, adsorbed, or absorbed

form. This assumption should be valid if the contaminant is converted from other forms to the dissolved state as evaporation continues.

ii. The vapor formed is in equilibrium with the liquid at the interface. This is a typical assumption in distillation design.

iii. The interface concentration is close to the bulk water concentration. This will depend on the relative rate of evaporation and diffusion or mixing of the soltuion. This assumption implies that as the compound evaporates from the upper layers, no concentration gradient exists. This assumption should hold in a completely mixed aeration tank.

iv. The water evaporation rate is unaffected by the presence of the contaminant or other surface-active agents. This assumption will not hold in wastewater systems because of the presence of colloidal material such as biomass and surfactants.

The water evaporation term (E) in Eq. 2 was estimated to be 2740 $g/m^2/day$. The half-lives of compounds released from a theoretical body of water (1 m deep and 1 sq. meter surface area) were determined (7). With these specifications, the estimated half-life of hexa-chlorocyclopentadiene (Hex) is 15 minutes. As can be seen from Equation 2, the half-life is directly proportional to the weight of water in the system (G). The weight of water is also directly proportional to the volume of the system since weight is the product

of density and volume. Thus, an aeration basin with its significantly larger volume than this 1 cubic meter model would have a much longer half-life for Hex or any other volatile compound due to evaporation losses from the surface.

Dilling et al. (8) compared their experimental evaporation rate results with the above equation for chlorinated compounds in dilute aqueous solutions and observed much longer evaporation half-lives than the calculated values. They suggested this variation was due to the non-uniform concentration near the surface of the water as the solute was depleted. The addition of peat moss (500 ppm) to the water, which served as a simulated organic content, initially accelerated the disappearance of the chlorinated compounds concentration in the water. At longer times, no further solute removal was noted. A decrease in the rate of disappearance of the chlorinated materials found at the longer times suggested a gradual release to solution of the chlorinated compounds from the peat moss. The MacKay and Wolkoff (7) and Dilling et al. (8) studies suggest that for evaporation from wastewater surfaces that the suspended solids adsorption may depress the rate of evaporation.

1.2.3.2 Air Stripping

The stripping action of the rising air bubbles generated by the aeration process causes release of volatile compounds to air. As the air bubble is formed, oxygen is transferred to the liquid and the volatile compounds may be transferred to the air bubble, which rises

to the surface and is released to the atmosphere. In activated-sludge systems with aeration, dilute concentrations of volatile compounds are frequently stripped (9).

Mass transfer due to air stripping can be considered as diffusion of the solute from the bulk liquid phase to the rising air bubble (10). The bulk liquid phase and rising air bubble are separated by an interface. Assuming no mass transfer resistance within this interface, the diffusive flux (gmole m^{-2} hr^{-1}) in each phase can be expressed as:

$$N = \Delta C * K \qquad \text{Eq. (3)}$$

where, N = Mass Flux (gmole m^{-2} hr^{-1}).

ΔC = Concentration Gradient or Difference (gmole m^{-3}).

K = Mass Transfer Coefficient (m hr^{-1}).

The mass transfer coefficient (K) can be thought of as the diffusion coefficient (m^2 hr^{-1}) divided by the diffusion pathlength (m). The reciprocal of the mass transfer coefficient is commonly called the resistance. The overall volatilization rate can be expressed as the summation of the resistances within the liquid and gas phase. However, for most compounds one phase resistance dominates.

The volatilization of hydrophobic pollutants from water bodies to the atmosphere has been described by a mathematical model approach using the Henry's Law constant, H which basically is the vapor pressure of the solute divided by the aqueous solubility of the solute (11). This can be expressed as follows:

$$H = P/C \qquad \qquad \text{Eq. (4)}$$

where H = Henry's Law constant ($atm\ m^3\ mole^{-1}$).

    P = Solute partial pressure in the air (atm).

    C = Aqueous Solubility of the Solute ($gmole\ m^{-3}$).

Mackay and Leinonen (12) developed the revelant equations relating the Henry's Law constant, H, to the mass transfer phenomenon, which are as follows:

$$N \qquad = K_{ol}(C - P/H) \qquad \qquad \text{Eq. (5)}$$

$$1/K_{ol} \qquad = 1/K_l + RT/HK_g \qquad \qquad \text{Eq. (6)}$$

where N   = Mass flux ($gmole\ m^{-2}\ hr^{-1}$).

    K_{ol}, K_l, K_g = the overall, liquid, and gas mass trans-

                 fer coefficient ($m\ hr^{-1}$), respectively.

    R   = Gas constant ($m^3\ atm\ gmole^{-1}\ {}^oK^{-1}$).

For compounds with H values greater than $5 \times 10^{-3}\ atm\ m^3\ gmole^{-1}$ (which implies high vapor pressure and/or low aqueous solubility) equations 4 and 5 reduce to:

$$N = K_l(C - P/H) \qquad \qquad \text{Eq. (7)}$$

and the mass transfer resistance dominates within the liquid phase. For compounds less than $5 \times 10^{-6}\ atm\ m^3\ gmole^{-1}$ (which implies low vapor pressure and/or high solubility) Equations 4 and 5 reduce to:

$$N = K_g(CH - P)/RT \qquad \qquad \text{Eq. (8)}$$

and the resistance dominates within the vapor phase.

MacKay et al. (11) developed an experimental method based on mass transfer of the solute within a stripping vessel to determine the

Henry's Law constant. The mass balance for the solute in terms of the transfer rate is as follows:

$$-V\frac{dC}{dt} = PG/RT = HGC/RT \qquad \text{Eq. (9)}$$

where   G   = Gas flow rate ($m^3\ hr^{-1}$).

   V   = Volume of the liquid within the stripping vessel (m^3).

   T   = System temperature ($^{\circ}K$).

Assumptions for this mathematical development include: i.) isothermal system, ii.) well-mixed liquid phase, iii.) ideal gas behavior, iv.) validity of Henry's Law over the tested concentration range, v.) low solute vapor pressure in comparison with the total system pressure, vi.) constant liquid volume and vii.) solute at the exit in equilibrium with the liquid. Equation 9 can be integrated with the initial condition at $t = 0$ of $C = C_0$, such that:

$$Ln(C/C_0) = -(HG/VRT)t \qquad \text{Eq. (10)}$$

where C_0 = Initial solute concentration at $t = 0$ ($gmole\ m^{-3}$).

   t   = Time (hrs).

Thus, the log of the concentration versus time plot should be linear with a slope of $-(HG/VRT)$. This slope can be considered a first order decay constant, Ka. The decay constant, Ka is directly proportional to the Henry's Law constant, H and if G, V, R. and T are kept constant during an experimental run, the decay constant can be calculated as:

$$Ka = HG/VRT \qquad \text{Eq. (11)}$$

The effects of suspended solids on the Henry's Law constant has not been evaluated (11) at this time. In a study of the stripping of acetone, the presence of suspended solids did not alter the first order decay constant (12). Thus, for acetone the Henry's Law constant does not appear to be affected by the presence of suspended solids. However, other compounds need to be evaluated, particularly compounds with less solubility in water, since these compounds may have a higher affinity for an organic matrix and become adsorbed. The effect of suspended solids on the Henry's Law constant or the decay constant under this situation is uncertain. As previously mentioned, aldehydes did not follow first order decay (3). Therefore, the MacKay et al. (11) experimental approach to determine the Henry's Law constant would not apply in this case, since the kinetic behavior was not first order.

1.2.3.3 Droplet Formation

A third mechanism of atmospheric release of a volatile compound is droplet formation. As the rising air bubbles break the wastewater surface, a cavity is formed, which is quickly filled because of surface tension and gravity. A rising jet of liquid is produced in this process, which has sufficient velocity to break away from the liquid surface and form into one or more droplets (13). Aerosol production in an activated-sludge unit with a porous diffuser (14) was affected by chemical composition of the liquid, buble stability, bubble size, air flow rate and rate of bubble production. The number of aerosols generated was found to increase with an increase in the bacterial content of the mixed liquor.

Once the droplets are expelled to the atmosphere, they can either fall back to the wastewater surface or evaporate and release their volatile components. If the droplet residues are less than ten microns in size, they will follow atmospheric currents and not readily settle out by gravity. Review of the literature suggest that the droplets quickly evaporate. However, this evaporation rate depends on the droplet size. Higgins (14) noted that the mean size of the droplets from an activated-sludge unit was 85 microns, which evaporated to a 5 micron mean droplet nuclei size. Wells (15) reported that droplets of 100, 50, 25, and 12 microns, were evaporated in 0.31, 0.08, and 0.02 seconds, respectively. The resulting droplet nuclei were 2 to 10 microns in diameter and normally contained one bacterium each. Webb (16) and Kenline (17) also reported rapid evaporation of the released aerosols. The Woodcook study (18) indicated bursting bubbles (20-200 microns) produced 2-200 microns droplets, which quickly evaporated to form droplet nuclei (1-45 microns). The droplet contained bacteria or material from the surface film. The liquid droplet could contain volatile compounds which are released to the atmosphere as the droplet evaporates to its solid nuclei. The volatile compounds could also be adsorbed on these bacteria nuclei or onto other particulate matter that is released from the aeration tank.

1.2.4 Factors Influencing the Release of Volatile Compounds from the Aeration Tank

The biomass in the aeration tank of the activated-sludge process may adsorb a volatile compound as it enters the system. The biomass

is carried to the clarifier and settled out. A portion is returned to the aeration tank. Because of the aeration process, stripping could desorb the volatile compound and release it to atmosphere. A mass balance of the aeration tank (as seen in Figure 1) for a volatile compound is as follows:

(Accumulation in Aeration Basin) = mass in - mass out - mass reacted - atmospheric release

$$C_a V_{t+\Delta t} - C_a V_t = C_i(I+R)\Delta t - C_a(I+R)\Delta t - K_d \Delta t - W_a \Delta t \quad \text{Eq. (12)}$$

where V = volume of the aeration tank (L).

C_a = the concentration of the volatile compound in the aeration tank and at the outlet by assuming the concentration is constant throughout the tank because of complete mixing (g/L).

I = the influent flow (Lpm).

C_i = the inlet concentration of the volatile compound (g/L).

R = the return sludge recycle flow (Lpm).

C_r = the return sludge cycle volatile compound concentration (g/L).

K_d = the overall kinetic degradation constant for the volatile compound, which describes the reaction kinetics and biodegradation (g/min.).

W_a = the emission rate of the volatile compound (g/min.).

t = initial time of the mass balance (min.).

Δt = the time over which the mass balance is being considered (min.).

$t + \Delta t$ = the final time of the mass balance application (min.).

The release of the volatile compound to the atmosphere will depend in part on the concentration of the volatile compound in the aeration unit, (C_a). If more of the organic is present in the aeration unit, then more is available for release to atmosphere. The increase in the return sludge recycle would provide more of the volatile for release. It is suspected that the increased solid matrix due to an increased recycling would affect the stripping rate of the volatile compound to atmosphere.

Kinetic degradation is specific for each volatile compound. Many volatile organics are degraded by the biomass. Some volatile compounds are initially toxic to the biomass and are then degraded after acclimation. The overall degradation constant of the volatile compound will depend on the compound, the biomass present, and on factors such as temperature, pH, light, biomass acclimation and history of exposure, and interaction with other toxic compounds. Thus, the kinetic degradation is not consistent over time but for simplicity of the above model, it is assumed to be constant.

Rising air bubbles in pure water have surface circulation. This circulation encounters fresh liquid on the top of the bubble, which is removed downward in relation to the bubble and the liquid leaves at the bottom. The presence of surface-active agents or organics produce a "skin" around the bubble that effectively prevents cir-

culation (19). This inhibited circulation will reduce the absorption rate of the volatile compound through the bubble-liquid interface. Conversely, surface-active agents and organic compounds will decrease the surface tension of the bubble-air interface which decreases the size of the bubbles generated from the air-diffuser. This in turn will increase the interfacial area available for transfer, which in some cases, will exceed the decreased mass-transfer coefficient and the overall-transfer rate could increase (20).

The concentration of surfactant has been shown to affect the transfer rate of oxygen from the rising air bubble to the wastewater Mancy and Okum (21) observed that a small amount of surfactant rapidly decreased the absolute transfer rate of oxygen. Increasing the surfactant concentration resulted in an observed minimum rate of oxygen transfer. Further increases in surfactant concentrations gradually increased the oxygen transfer rate. In similar fashion, surfactant concentration could affect the transfer of the volatile compound to the rising air bubble.

In summary, many variables influence the release of the volatile compound from the aeration tank to atmosphere, such as kinetic reactions, adsorption onto suspended solids, partition into any nonaqueous liquid phases, desorption from the solid matrix, and volatilization into the rising gas bubble. Surfactants may affect the release from the aeration tank liquid surface, reduce the bubble size and inhibit the mass-transfer rate through a bubble. In addition, toxic compounds could alter the biomass and influence its ability to adsorb organic compounds.

1.2.5 Emission Rate Estimation from the Mass Balance

If a test component is released to the atmosphere from a process unit, the wastewater concentration should decrease over time. Collection of wastewater samples over a specified time and analysis for the test component concentrations could lead to an emission rate determination. However, this technique to determine the emission rate of a component from a process unit depends on the uniform distribution of the component throughout the process unit (22). This mass balance technique to determine the emission rate was developed for two process units at an activated-sludge plant: the aeration basins and the grit-chamber weir.

1.2.5.1 Aeration Basin Mass Balance

The previous sections described the mass balance of a volatile compound in an aerated basin and factors that affect the release of the volatile compound to atmosphere. Rearrangement of Eq. 12 will yield a method to estimate the emission rate of volatile compound from the aeration basin:

$$W_a = \frac{-C_a V_{t+\Delta t} - C_a V_{\Delta t}}{\Delta t} + C_i(I+R) - C_a(I+R) - K_d \qquad \text{Eq. (13)}$$

For highly chlorinated compounds such as Hex, biodegradation of the compounds is unlikely. Cole (23) noted Hex was an extremely effective bacteriocide and that it was twice as effective in killing Salmonella Typhosa, a typical sewage bacteria, and fecal coliform, than equivalent concentrations of chlorine. Also, assuming that these compounds

are conservative (no chemical reactions), the K_d term is zero. Thus, simple measurements of the influent and effluent mixed liquor concentrations of the volatile compound in the aeration basins, and knowledge of the flow rates of the influent and return sludge could be sufficient to estimate the emission rate. The mixed liquor of the aeration basins would be collected at time, t and time $t + \Delta t$, which will be analyzed to determine C_a at time, t and $t + \Delta t$.

1.2.5.2 Grit-Chamber Weir Mass Balance

Another location within the sewage treatment plant of concern with respect to atmospheric release (besides the aeration basins) is the grit-chamber weir. Raw sewage flows at high velocity over the weir. Figure 2 shows the side and top view of a grit-chamber weir at the North Sewage Treatment Plant, Memphis, TN. A simplified mass balance of this situation is as follows:

$$W_b = C_1 Q_w - C_2 Q_w \qquad \text{Eq. (14)}$$

where W_b is the atmospheric emission rate of the volatile
compound (g/min.).

C_1 is the concentration of the volatile compound
in the raw sewage just above the weir (g/L).

C_2 is the concentration of the volatile compound
in the raw sewage just below the weir (g/L).

Q_w is the flow rate of the raw sewage (Lpm).

1.2.6 Emission Rate Calculations from Air Sampling Data

1.2.6.1 Aeration Basin Atmospheric Dispersion Model

Air sampling at various locations above the aeration basins will provide a weight of the collected contaminant which corresponds to a known volume of air. The air sampler passes a known volume of air through a sorbent tube, which is later analyzed to obtain a weight of the contaminant. If it is assumed that the collected air is only air released from the aeration basins and not air dispersed from adjacent non-aerated surfaces, then the following atmospheric box dispersion model is valid:

$$W_C = \frac{\Sigma \text{Air Sampler Comtaminant Weight}}{\Sigma \text{Air Sampler Volume of Collected Air}} \times Q_a \qquad \text{Eq. (15)}$$

where W_C is the emission rate of the aeration basins based

on air sampler data (g/min.).

Q_a is the air flow through the aeration basins (Lpm).

Because of the box-model assumption, this calculated emission rate is highly depended on wind speed and should only be considered as an order of magnitude comparison with the mass balance estimate.

1.2.6.2 Grit-Chamber Weir Line Source Atmospheric Dispersion Model

The release of a contaminant from the grit-chamber weir will be generated from a line source as described in the top view of Figure 2. A line source atmospheric dispersion model is necessary to provide a calculated emission rate from the air sampler data. Figure 3 describes the line source atmospheric model of Sutton (24). This gaussian distribution dispersion model was further developed by Turner (25) and is as follows:

$$C(X,Y,Z,H) = C(X,0,0,0) = \frac{2q}{\sqrt{2\pi}U\sigma_z} \int_{P_1}^{P_2} \frac{1}{\sqrt{2\pi}} \exp(-0.5P^2) \, dP$$

Eq. (16)

where $C(X,Y,Z,H)$ is the concentration of the contaminant at

the air sampler location, X meters downwind from the

line source.

$Y = 0$ implies that the air sampler is located on the

centerline perpendicular to the line source.

$Z = 0$ implies that the air sampler is located at the

same height of the line source.

$H = 0$ implies that there is no plume rise of the

contaminante release from the line source.

q is the emission rate (g/m-sec), which is re-

lated to the desired emission rate, W_d.

W_d is the calculated emmission rate from the grit

chamber weir (g/sec) where $W_d = qxL$.

L is the length of the line source and is equal to

$Y_2 - Y_1$ (m).

U is the wind speed perpendicular to the line source

(m/sec).

σ_Z, σ_Y are the standard deviations of the distribution of

the contaminant in the plume cross wind in the

horizontal (Y) and vertical (Z) direction.

The value of σ_Z and σ_Y depend on the downwind direction (X) and the

atmospheric stability class. Turner (25) presented graphs to determine

σ_Z and σ_Y as a function of X, the downwind direction and stability class. The stability class is estimated from the wind speed and during the day, the incoming insolar insolation or, during the night the cloud cover. The integral presented in Eq. 16 is found in standard statistical tables (25) where $P_1 = Y_1/\dot{\sigma}_Y$ and $P_2 = Y_2/\sigma_Y$. Thus Eq. 16 can be arranged to find the emission rate:

$$W_d = qxL = \cfrac{C(X,0,0,0)\ 2U\sigma_z L}{\int_{P_1}^{P_2} \frac{1}{\sqrt{2\pi}}\exp(0.5P^2)dP} \qquad \text{Eq. (17)}$$

The atmospheric dispersion model relies on σ_Y and σ_Z values which are only approximations. The value of σ_Z can vary by a factor of 2. Turner (25) felt the uncertainties of σ_Y were considerably less.

2.0 EXPERIMENTAL METHODS

The study was comprised of two aspects: field surveys of an activated-sludge sewage treatment plant and a laboratory model aeration basin of an activated-sludge sewage treatment plant study. The field studies were designed to evaluate the wastewater and airborne concentrations of three chlorinated compounds: hexachlorobicycloheptadiene (Hex-BCH), heptachlorobicycloheptene (Hex-VCL), and chlordene at various locations of the North Sewage Treatment Plant, Memphis, Tennessee. The wastewater samples were collected to demonstrate the receipt of these test compounds in the influent as well as to determine their distribution or fate in the plant. The air samples were collected at the various locations to establish the level of atmospheric release. Initial aeration unit experiments were conducted to determine the stripping kinetic behavior of Hex-BCH from aqueous solutions and to develop an adequate simulated wastewater solution and laboratory aeration unit. The developed bench-scale aeration unit was used to evaluate the influence of aeration rate, suspended solids concentrations and detergent level on the atmospheric release of two chlorinated compounds (Hex-BCH and chloroform).

2.1 Field Studies

The field studies consisted of several field surveys of the North Sewage Treatment Plant, Memphis, Tennessee, as listed in Table 1. This facility received both municipal and industrial waste. The industrial wastes are from several types of industries but the waste

from one manufacturer included several chlorinated precursors of
pesticides and flame retardants such as Hex, chlordane, chlordene,
aldrin and isodrin. Only three test compounds (Hex-BCH, Hex-VCL and
chlordene) were selected for monitoring this activated-sludge sewage
treatment plant.

Unless otherwise stated, all air samples were for four hours with
a single grab wastewater samples at the midpoint of the survey. Each
survey included meterological observations as to weather, wind
direction and speed. The first five surveys were completed March
22-24, 1979 and the latter five surveys were completed September 11-13,
1979. The wastewater and air samples were analyzed by the procedures
described in Appendix 7.1.

2.1.1 Description of the North Sewage Treatment Plant, Memphis,
      Tennessee

The field studies were conducted at the north activated-sludge
sewage treatment plant in Memphis, Tennessee. As shown in Figure 4,
a physical layout of the plant, the plant is divided into two
identical batteries of aeration basins. Each battery consists of
three contact basins, six stabilization basins and three aerated
digesters. As shown in Figures 4 and 5, a flow diagram of the plant,
the primary treatment of the wastewater began with coarse screening of
the influent raw sewage in the wet-well. The screened raw sewage is
pumped to the grit chambers and filtered through a series of fine
screens. The filtered raw sewage then enters the four grit chambers
where sand and grit are allowed to settle. The solids from the coarse

and fine screens, and the grit chambers are conveyed into dumpsters
for later landfill disposal.

Activated-sludge treatment began with raw sewage entering the
raw sewage basin at the upstream (east) end of the aeration basins
which then proceeds into the return activated-sludge basin. Here it
will mix with return activated-sludge from the stabilization basins.
This mixed liquor flows by gravity to the contact aeration basins.
After one to three hours in the contact basins, the mixed liquor flows
in open channels to fourteen secondary clarifiers. The supernatant
from these clarifiers flows through the chlorine contact basins (no
chlorination is currently practiced) and is discharged into the
Mississippi River as final effluent. The settled sludge from these
clarifiers is pumped to the sludge building. A major portion of this
sludge (return sludge) is pumped to the stabilization basin and the
remainder (waste sludge) is pumped to the digesters. The retention
time in the stabilization basins is 10-12 hours. After aerobic di-
gestion of approximately 11 days, the digested waste sludge flows to
either of two sludge thickeners and the thicken-sludge is pumped to
the storage lagoons. The lagoons are located at the north end of the
plant. The supernatant from the lagoons and the sludge thickeners
is returned to the wet-well and is processed through the plant again.

Air is forced through diffusers at the bottom of each contact
basin, stabilization basin and digester to supply needed oxygen for
the biomass. This air was pulled from the atmosphere at air intakes
located on top of the blower house building, as shown in Figure 4, and

forced through the plant by centrifugal blowers. This air was carried through an underground pipe galley to each of the aeration basins. For each day that was surveyed, the aeration rate as well as the suspended solids level for each aeration basin type: contact, stabilization and digester, is presented in Table 2.

2.1.2 Atmospheric Release Surveys (I,II,III)

The purpose of these surveys (I, II and III) was to determine the airborne release of the Hex-related compounds at various locations of the plant during day and night conditions. In addition, the Clear Day Survey (II) was designed to determine if the release of Hex-related compounds from the aeration basins was drawn into the intakes of the aeration system located on the top of the blower house building. If this were to occur, this may result in a recycling effect, i.e., the stripped compounds that are released to the atmosphere from the aeration basins may be reintroduced into the wastewater by the aeration process. Survey I was conducted during a rainy day, Survey II during a clear day and Survey III during a clear night.

Survey I was curtailed to two hours to protect the sampling equipment. The wastewater and air sampling locations of the Rainy Day Survey (I) are shown in Figure 6. To determine the receipt and distribution of the Hex-related compounds in the plant, the wastewater samples were collected at the wet-well (WS #1), grit-chamber (WS #2), lagoon effluent (WS #3), two digesters (WS #4 and 5) and in the final effluent (WS #6). All air sampling locations were outside where sample

concentrations are influenced by meteorological conditions such as wind direction and speed. The grit chamber (AS #1), three locations at the aeration basins (AS #2, 3, and 5), and two locations at the lagoon (AS #4 and 6) were sampled.

The air and wastewater sampling positions of the Clear Day Survey (II) are shown in Figure 7. Wastewater samples included wet-well (WS #1), grit-chamber (WS #2), contact basin (WS #3), stabilization basin (WS #4), digester (WS #5), and the final influent (WS #6). The air sample collections included two on top of the blowerhouse building, which is approximately 40 feet above the ground (AS #1 and 2), center and east end of the aeration basins (AS #3 and 4), grit-chamber (AS #5) and wet-well (AS #6).

The wastewater and air sampling locations of the Clear Night Survey (III) are shown in Figure 8. The wastewater samples included wet-well (WS #1), grit-chamber (WS #2), Battery B digester (WS #3), Battery B stabilization basin (WS #4), Battery B contact basin (WS #5) and the final effluent (WS #5). The air samples included grit-chamber weir (AS #1), grit-chamber drag-out (AS #2), west end of the aeration basins (AS #3), center of aeration basins (AS #4), and east end of the aeration basins (AS #5). The wastewater and air samples for this survey were also analyzed for chloroform, carbon tetrachloride and tetrachlorethylene.

2.1.3 Aeration Basins Survey (IV)

The purpose of this Aeration Basins Survey (IV) was to determine

the airborne levels of the Hex-related compounds at the three different

types of aerations basins: contact, stabilization and digester and to

evaluate the influence of aeration rate and suspended solids level on

the atmospheric release of Hex-related compounds. Each aeration basin

type was of the same size and shape but varied in their aeration rate

and suspended solids concentration (See Table 2 for specific levels).

The wastewater and air sampling locations are shown in Figure 9. The

wastewater samples included the wet-well (WS #1), grit-chamber (WS #2),

west end of aeration contact basins (WS #3), west end of stabilization

basins (WS #4), west end of digester (WS #5), center of digester (WS #6),

center of stabilization basins (WS #7) and center of digesters (WS #8).

The air sampling positions were upwind of the contact basins (AS #1),

stabilization basins (AS #2) and digesters (AS #3) as well as downwind

at the midpoints of the digesters (AS #4), stabilization basins (AS #5)

and contact basins (AS #6).

2.1.4 Confined Spaces Survey (V)

The purpose of this survey (V) was to determine if the concen-

tration of Hex-related compounds would increase in the atmosphere of

the confined spaces of the plant. This location of the wastewater

and air samples are shown in Figure 10. Wastewater samples were

collected at the wet-well (WS #1), grit-chamber (WS #2), lagoon in-

fluent (WS #3), two digesters (WS #4 and 5) and in the final lagoon

influent (WS #6). Air samples (AS #1, 2 and 3) were collected in the

pipe galley, approximately 30 feet underground, beside the walls of

the aeration basins and at the wet-well (AS #4), which is where the plant influent enters the plant. The wet-well is exposed to the atmosphere but any released volatile compounds can be confined in the wet-well building. Two air samples (AS #5 and 6) were collected in the maintenance and administrative office. The first air sample (AS #5) was collected in the intake duct of the building ventilation system. The second air sample (AS #6) was collected at the ventilation duct opening in the plant operation control room. The purpose of the AS #5 and 6 samples was to determine if the Hex-related compounds released to the atmosphere from various areas of (i.e., aeration basins or grit-chamber weir) reached the main worker area of the plant.

2.1.5 Clarifiers and Lagoons Survey (VI)

The purpose of this Clarifiers and Lagoons Survey (VI) was to specifically evaluate the airborne release of the Hex-related compounds from the clarifiers and lagoons. As seen in Figure 4, at this plant there are fourteen clarifiers which are divided into two separate sets of seven clarifiers to handle each battery of aeration basins. The wastewater and air sampling locations are shown in Figure 11. Each of the six clarifiers sampled for wastewater had a corresponding air sample (A #1-6 and W #1-6). All clarifier wastewater samples were taken about five feet from the center of the clarifier, which is where the mixed liquor influent from the contact basins entered. These wastewater samples were collected approximately six inches below the mixed-liquor surface. At each of the north and south lagoon sampling locations

for wastewater (WS #7 and 8) two corresponding air samples (AS #7 and 9) and (AS #8 and 10) were collected. One air sample was collected on Chromosorb 102 and an adjacent air sample was collected on charcoal.

2.1.6 Mass Balance Surveys of the Contact Aeration Basins (VII,VIII)

The first purpose of these two surveys (VI,VIII) was to evaluate if a mass balance technique to estimate the emission rate of the Hex-related compounds from the contact aeration basins was valid. The second purpose was to compare these emission rates with the emission rate calculated from the air sampling data incorporated in the at-mospheric box dispersion model (as described in Section 1.2.6.1). The wastewater and air sampling locations for the morning survey (VII) and the afternoon survey (VIII) are shown in Figures 12 and 13, respectively. The 100 mL single grab wastewater samples were collected from the surface of the inlet channel (WS #1 and 2), contact aeration basins (WS #3-6) and the outlet channel (WS #7 and 8). The air samples were collected approximately one and one-half feet above the wastewater surfaces of the aeration basins (AS #1-4). The wastewater was initially sampled at each site and sampled again after completion of a 0.5 hour air sampling survey. The box model calculated emission rate was determined from the air sampling data and with knowledge of the air flow rate through the contact aerations (Eq. 15). The effect of wind was minimized by placing the air sampling adsorbent tubes within two feet above the wastewater surfaces of the contact basins. The placement of the ad-sorbent tubes at these locations assured that the air samples was primarily air released from the contact aeration basins.

2.1.7 Mass Balance Surveys of the Grit-Chamber Weir (IX,X)

The first purpose of these two surveys (IX and X) was to evaluate if the mass balance technique to estimate the emission rate of the Hex-related compounds from the grit-chamber weir was valid.   The second purpose was to compare these emission rates with the emission rates calculated from the air sampling data incorporated in the atmospheric line source model (as described in Section 1.2.6.2). The wastewater and air sampling positions of the afternoon survey (IX) and the morning survey (X) are shown in Figure 14. Four 100 mL wastewater grab samples were collected. Two sampling positions were upstream of the grit-chamber weir (WS #1 and 3) and the other two positions were downstream of the weir (WS #2 and 4). Immediately after the initial wastewater sampling, the air sampling survey was conducted for 0.5 hours. A final 100 mL grab sample was taken from each of the same four wastewater sampling locations. The air sampling locations (AS #1-3) were on a catwalk approximately 30 inches above the grit-chamber wastewater surface. These air sampling positions were in a straight line per-pendicular to the weir, so that the atmospheric dispersion line source model could be applied to yield a calculated emission rate.

The atmospheric dispersion line source model was developed for es-timation of three to fifteen minutes average concentration values. A technique to correct the 0.5 hour air sample concentration values to the three to fifteen minute concentration estimates required in the line source model has been developed (26). Analysis of the wastewater samples, application of the mass balance as described in Eq. 14, and

the atmospheric model as described in Eq. 17 were completed to determine the validity of the mass balance approach to estimate the emission rate from the grit-chamber weir.

2.2 Laboratory Aeration Unit Studies

Initially a series of experiments were performed to determine how Hex-BCH was stripped by aeration from aqueous solution. The second part included development of a synthetic wastewater solution as well as development of a bench-scale laboratory aeration vessel to simulate the aeration basin of an activated-sludge sewage treatment plant. This system was used to evaluate the influence of aeration rate, suspended solids and detergent concentrations on the atmospheric release of two chlorinated compounds: Hex-BCH and chloroform ($CHCl_3$).

2.2.1 Initial Experiments

The four initial experiments with Hex-BCH are summarized in Table 3. The first experiment was conducted with double distilled water (DDW) in a two liter Erlenmeyer flask. The Hex-BCH (20 uL) was combined with one liter of DDW and stirred for at least two hours to assure uniform Hex-BCH distribution. The next two experiments were completed with suspended solids, which was Whatman Column Chromedia (CF-11-fibrous cellulose powder). The suspended solids (500 and 5000 mg/L) and 20 uL of Hex-BCH were combined with one liter of DDW and stirred for at least two hours to assure uniform suspended solids and Hex-BCH concentration. In the last Hex-BCH experiment, a filtercake was used as the suspended solids, which was a biologically-digested vacuum-filtered activated-

sludge from the Mill Creek Sewage Treatment Plant, Cincinnati, Ohio. The sludge was further vacuum and heat dried in the labaoratory, sifted through a Tyler 30 mesh screen and homogenized in a small amount of DDW for 1-2 minutes. In this filtercake experiment, the aer..ion vessel was a five liter round bottom flask.

Aeration was provided by nitrogen, which was blown through a fritted glass bubbler. The fritted glass bubbler was located at the bottom of the aeration vessel. A magnetic stirrer was used to maintain the suspended solids and prevent settling. After aeration was begun, 5 mL aliquots of the mixture were drawn immediately, and at 0.5, 1, 2, 3, 4, 5, and 6 hours of aeration. The aeration rate of nitrogen was maintained at 35 cc/min and was monitored by a soap bubble meter. The experiments were conducted at room temperature of approximately $25^{\circ}C$.

Another initial experiment was conducted with chloroform. The chloroform (20 uL) was added to two liters of DDW at $25^{\circ}C$ in a two liter round bottom flask and stirred overnight prior to an aeration experiment at 35 cc/min. Wastewater aliquots were drawn at 0.25, 0.5, 1, 2, 3, 4, 5, and 6 hours of aeration and analyzed for chloroform.

2.2.2 Bench-Scale Aeration Unit Experiments

A bench-scale aeration system was developed in order to determine the role of three parameters, aeration rate, suspended solids and detergent concentrations, on the stripping of Hex-BCH and chloroform from a simulated wastewater solution. The laboratory apparatus shown in Figure 15 consisted of duplicate systems to allow simultaneous com-

pletion of two experimental runs. A two liter three neck round bottom
flask served as the aeration vessel. Nitrogen was introduced through
the center port in a fritted-glass bubbler. The outside port contained
a wastewater sampling tube, which allowed convenient collection of the
wastewater aliquots without interrupting the aeration experiment. The
inside port was connected to an adsorbent tube, which collected the
stripped Hex-BCH and $CHCl_3$ present in the off-gas. The simulated
wastewater (2 L) was prepared by adding 20 uL of Hex-BCH and 20 uL
of $CHCl_3$ to two liters of DDW and stirred overnight. This solution was
filtered to remove undissolved Hex-BCH. Homogenized filtercake sludge
and detergent were added to this solution and the mixture was stirred
overnight again to assure uniform distribution. The detergent used
was standard linear alkylate sulfonate (LAS) which was supplied by the
U.S. Environmental Protection Agency (Cincinnati, Ohio). Aeration was
initiated and 5 mL wastewater samples collected after 0.25, 0.5, 1, 2,
3, 4, 5, and 6 hours of aeration. After no more than an half hour,
the wastewater aliquots were extracted (See Appendix 7.1 for the pro-
cedure). The gas chromatograph with electron capture detector (GC/ECD)
analysis was conducted at 175°C for Hex-BCH and 60°C for $CHCl_3$. A
linear regression model was completed on the log of the wastewater
concentration values versus time for both compounds. The first order
kinetic decay constant and corresponding correlation coefficient were
determined by a calculator program, which is described in Appendix 7.2.
Five aeration rates, three suspended solids concentrations and three
detergent levels were used in this laboratory study (Table 4). All

possible combinations were investigated (5 x 3 x 3) and each of the 45

experiments was duplicated. The three factors (aeration rate, solids

suspended concentration and detergent level) were evaluated with a three-

way analysis of variance (ANOVA). This analysis was completed on each

compound (Hex-BCH and $CHCl_3$) with the log_{10} of the decay constant as

the response variable. This statistical method will indicate if any

of the interactions are significant. Also, because it is assumed

that each factor is fixed, there is an exact test for the significance

of each factor (27).

The adsorbent tube of Chromosorb 102 which was placed in the

exit gas line of the aeration vessel in the bench-scale system (Figure

15) trapped the Hex-BCH and $CHCl_3$ stripped from the simulated waste-

water solution. The adsorbent tube was desorbed with 2 mL of petroleum

ether (PE) and analyzed as described in Appendix 7.1. The analysis

yield a concentration for both Hex-BCH and $CHCl_3$. The adsorbed weight

of Hex-BCH and $CHCl_3$ was determined as follows:

$$\text{Collected/Desorbed Weight, mg} = \text{Concentration } \frac{(ng)}{\text{mL PE}} \times 2 \text{ mL PE} \times$$

$$10^{-6} \frac{mg}{ng} \qquad \text{Eq. (18)}$$

The total amount of Hex-BCh or $CHCl_3$ stripped form the wastewater

solution was calculated from a mass balance, as follows:

$$\text{Total Amount} = (\text{Initial - Final}) \text{ Wastewater } \frac{ng}{mL}$$
$$\text{Stripped, mg} \qquad\qquad\qquad \text{Concentration}$$

$$\times 2000 \text{ mL Wastewater} \times 10^{-6} \frac{ng}{mL} \qquad \text{Eq. (19)}$$

The collection/desorption efficiency or recovery fraction was determined as follows:

Recovery Fraction = $\dfrac{\text{Collected/Desorbed Weight, mg}}{\text{Total Amount Stripped, mg}}$ Eq. (20)

The mean recovery fraction was calculated for each aeration rate to determine the influence of flow rate on the collection/desorption efficiency of Hex-BCH and $CHCl_3$ on Chromosorb 102.

3.0 RESULTS

3.1 Field Studies

The variation in wastewater concentrations of several chlorinated organic compounds at the North Sewage Treatment Plant, Memphis, Tennessee over a one-month period (July-August, 1978) is presented in Table 5. This data illustrates continuous flow of Hex-BCH, Hex-VCL and chlordene to this plant. The mean influent concentrations were 454, 99 and 197 ng/mL, respectively. The high concentration of these substances in the sludge (6138, 1277 and 265 ng/mL, respectively) suggests significant adsorption by the suspended solids. The final effluent levels were reduced to 60, 9, and 15 ng/mL, respectively. The plant effluent concentrations were reduced because of airborne release and the suspended solids separation in the clarifiers. The adsorption of the test compounds to the suspended solids results in their return to the aeration basins following solids separation in the clarifiers.

3.1.1 Pooled Wastewater Analysis Data from March 22-24, 1979

The wastewater concentration of the tested compounds at various locations throughout the plant over the March 22-24, 1979 test period (Surveys I-V) are shown in Table 6. The highest mean concentration of these compounds was found in the sludge of the digesters (449, 385, 3925 ng/mL for Hex-BCH, Hex-VCL and chlordene, respectively). This suggests significant adsorption to the suspended solids. Because of the airborne release and suspended solids separation in the clarifiers, the plant effluent concentrations were drastically reduced (6, 3, and 78 ng/mL, respectively). The trend of significant reduction of the con-

centrations of the test compounds from the aeration basin wastewater
to the final effluent, which was evident from the data presented in
Table 5 for the July-August, 1978 samples was again observed in the
March 22-24, 1979 surveys.

The plant influent flow and the wastewater concentrations of Hex-
BCH, Hex-VCL and chlordene during the March 22-24, 1979 Surveys (I-V)
are shown in Table 7. The data shows a relatively consistent influent
flow rate (3.42 to 4.6 2 x 10^8 L/day) and a slight variation in the
Hex-BCH (21-79 ng/mL) and Hex-VCL (8-27 ng/mL) concentrations. The
chlordene influent concentration had a peak of 821 ng/mL at 7:00 P.M.
on March 22, 1979 which decreased to 63 ng/mL by 11:00 A.M. of the
next morning. It appears that a spike flow of chlordene probably
occurred on this day.

To determine if aerated sources of the activated-sludge plant
such as the aeration basins yield higher airborne releases than non-
aerated sources, such as the grit-chamber weir, a comparison of results
from the adjacent air and wastewater sampling locations was done. The
results from the March 22-24, 1979 surveys are presented in Table 8.
Airborne release appears to be more significant for these compounds
from the aerated sources such as the contact basins or digesters than
other locations in the plant. The airborne concentrations of Hex-BCH
at the contact basins ranged from 10.3 to 22 ng/L whereas samples
collected at the grit-chamber area ranged from non-detected to 5.0 ng/L.
Airborne concentrations of Hex-VCL at the contact basin ranged from
3.0 to 6.7 ng/L and at the grit-chamber area from 0.03 to 1.0 ng/L.

The chlordene airborne concentrations at the contact basins ranged from 21.3 to 26.1 ng/L and only 0.2 to 3.3 ng/L in the grit-chamber area. The suspected chlordene spike flow of March 22, 1979 probably caused a build up of this compound in the sludge of the aeration basins (1600 to 3200 ng/mL). This sludge concentration of chlordene was higher than either of the Hex-BCH (86 to 440 ng/mL) or the Hex-VCL (58 to 390 ng/mL). This could explain the much higher airborne levels of chlordene found at the aeration basins. Since all three test compounds concentrate in the aeration basins there is a greater potential for atmospheric release in this area of the plant than from areas such as the grit-chamber. Furthermore, the aeration in the contact basins or digesters provided a mechanism to enhance the airborne release of the test compounds.

3.1.2 Atmospheric Release Surveys (I,II,III)

Three atmospheric release surveys (I,II,III) involved measurements of airborne concentrations outdoors under different meterological conditions. In all three surveys the prevailing wind was from the west. Survey I was conducted during daylight under rainy conditions. When the survey began an intermittent rain was falling which later turned into a heavy downpour. This weather change forced termination of the survey after only two hours. Survey II was conducted during a clear day and Survey III during a clear night. These two surveys lasted for four hours.

The wastewater concentrations for Survey I are reported in Table

9. As observed previously, the test compounds tended to concentrate in the aeration basin sludge. As seen in Table 10, the air sampling locations near the non-aerated sources such as the grit-chamber, north and south lagoon yield low airborne Hex-BCH concentrations (non-detected, 0.3 and 0.3 ng/L, respectively). Air sampling locations near aerated sources such as the north, center and east sections of the aeration basins yield higher airborne Hex-BCH concentration (21.7, 18.2 and 3.6 ng/L, respectively. A similar trend was noted for Hex-VCL and chlordene.

The wastewater concentrations for the second survey (II) are presented in Table 11. The airborne concentrations for the aeration basins were for Hex-BCH (11.3 and 9.6 ng/L), for Hex-VCL (3.0 and 2.7 ng/L) and for chlordene (25.4 and 21.7 ng/L) (Table 12). In addition, two air samplers were placed on top of the blowerhouse building at the air intakes to determine whether atmospheric releases from the aeration basins were recycled back to these basins via the aeration system. The airborne levels at the blowerhouse air intakes were quite low for Hex-BCH (0.3 and 0.1 ng/L), for Hex-VCL (0.08 and 0.04 ng/L) and for chlordene (0.3 and 0.2 ng/L). This indicates minimal recycling of the contaminants which are released from the aeration basins. This could be due to the prevailing wind from the west pushing any atmospheric release away from the blowerhouse air intakes. Secondly, since the air intakes are approximately 40 feet above the aeration basins, there is a significant decrease in airborne concentration with height due to atmospheric dispersion.

The results of the third survey (III) are presented in Table 13 for the wastewater concentrations and in Table 14 for the airborne concentrations. The airborne release at the grit-chamber weir for Hex-BCH (5.0 ng/L) and Hex-VCL (1.0 ng/L) were as high as the release from the west end of the aeration basins (3.6 and 0.85 ng/L, respectively). With a downwind buildup, the airborne levels at the east end of the aeration basins were much higher (18.7 and 4.8 ng/L).

More water-soluble chlorinated hydrocarbons such as chloroform ($CHCl_3$), carbon tetrachlordie (CCl_4) and tetrachloroethylene (TCE) were analyzed in the wastewater and air samples of survey III. These more water-soluble compounds, as seen in Table 15 for the wastewater concentrations, did not adsorb onto the sludge. As an example, $CHCl_3$ wastewater concentration was 19 ng/mL in the wet-well and only 5 ng/mL in the digester. In atmospheric sampling, as seen in Table 16, the grit-cahmber weir sample yield the highest airborne $CHCl_3$ concentration (5.8 ng/L) whereas the east or downwind aeration basin concentration was lower (2.6 ng/L). A similar trend was observed with CCl_4 and TCE airborne levels.

3.1.3 Aeration Basins Survey (IV)

This survey was conducted to determine whether the variation in aeration rate and suspended solids of the different aeration basin types: contact, stabilization, or digester affected the atmospheric release of the Hex-related compounds.

Atmospheric release of the test compounds occurred at all aeration basins. The wastewater results indicate that the compounds tend to concentrate in the aeration basins. The plant effluent concentration of Hex-BCH and Hex-BCL are at least 80% less than the influent levels. Chlordene levels were not reduced. As seen in Table 17, the concentration of Hex-BCH and Hex-VCL in the wastewater increased as the wastewater flowed through the plant from the contact basins (132 and 97 ng/mLO to the stabilization basins (278 and 220 ng/mL) and finally the digesters (428 and 378 ng/mL). In contrast, a lower chlordene concentration was found in the wastewater of the digesters (4016 ng/mL) than either of the contact (4598 ng/mL) or the stabilization (6078 ng/mL) basins. This may be due to the higher influent level of chlordene which occurred two days prior to the survey. This spike flow had sufficent time to reach the contact and stabilization basins (10-12 hours) but not adequate time to affect levels in the digesters, which have a retention time of 11 days. Airborne concentrations tended to increase in a downwind direction (Table 18). During the survey the wind direction was predominately from the west. The downwind (east) air sampling locations at the midpoint of the aeration basins had higher concentration levels than upwind locations. As an example, the upwind airborne concentration of Hex-BCH at the contact basin was 1.4 ng/L and the downwind concentration was 27.0 ng/L. For each compound, the higher airborne concentrations were found over the contact and stabilization basins, whereas lower airborne levels were found over the digesters. As an example for Hex-BCH, the contact and stabilization basins down-

wind concentrations were 27.0 and 16.0 ng/L. For the digester, the downwind concentration for Hex-BCH was 6.4 ng/L. As seen from Table 2, for the day of the Aeration Basins Survey (March 24, 1979) the much higher air flow through the contact and stabilization basins (91 and 100 KCFM, respectively) as compared to the 31 KCFM flow through the digesters could partially account for this. In addition, the stabilization and digester basins have much higher suspended solids levels (13,000 and 12,300 mg/L, respectively) than the contact basins (4,400 mg/L), which suggests that higher suspended solids levels may suppress the aerial stripping.

3.1.4 Confined Spaces Survey (V)

This survey was conducted to determine if airborne concentrations of Hex-related compounds would increase in confined areas of the plant (Figure 10). The wastewater Hex-related concentrations for this survey are reported in Table 19. The airborne concentrations (Table 20) for all three compounds found in the three underground pipe galley locations tend to build in concentration toward the eastern end of the aeration basins. As an example, the Hex-BCH airborne concentrations at the west, center and east pipe galley locations were 2.4, 6.1, and 11.4 ng/L, respectively. The prevailing wind during this survey was from the west, which could carry atmospheric releases of the test compounds toward the eastern end of the plant. Furthermore, during this survey there was an intermittent rainstorm. This rain could have suppressed the natural rising air currents thereby enhancing the airborne levels in the pipe galley. Contamination of the pipe galley was probably

through the open galley doors, which allow access to gound level. Two
air samples collected at the administrative building practically yielded
identical airborne concentrations for Hex-BCH (1.3 and 1.3 ng/L), for
Hex-VCL (0.3 and 0.2 ng/L) and for chlordene (0.6 and 0.5 ng/L). One
sample, collected at the intake of the ventilation system to the building,
samplec air coming directly from outside. The second sample collected
air adjacent to the ventilation duct in plant operation control room,
which is manned 24 hours a day. There was essentially no difference
between indoors and outside air. These results suggest that the filters
of the ventilation system were ineffective in removing the organic
vapors.

3.1.5 Atmospheric Release from the Clarifiers and Lagoons (Survey VI)

The extent of atmospheric release of Hex-related compounds from
the clarifiers and lagoons was evaluated on September 11, 1979. As
shown in Table 21, the concentration of compounds in the wastewater
samples from the six clarifiers ranged from 45 to 7200 ng/mL for Hex-
BCH, from 9.5 to 500 ng/mL for Hex-VCL and from non-detected to 54
ng/mL for chlordene. It is apparent that low levels of chlordene were
present in the wastewater samples collected from the clarifiers during
this survey. The wide range of wastewater concentration for Hex-BCH
and Hex-VCL may be due to variation in the sludge concentration in-
herent in the grab wastewater samples. As pointed out earlier, the
sludge that settles out in the clarifiers is returned to the stabili-
zation basins and digesters. Thus, since the Hex-related compounds

are adsorbed onto the sludge, the wastewater samples of the settling

sludge may result in higher reported concentrations of Hex-BCH and Hex-

VCL. The supernatant, on the other hand, contains less solids and con-

sequently would be expected to have a much lower concentration. Although

all wastewater samples were near the surface, non-homogeneous mixing may

result in samples containing different amounts of sludge which woulc be

reflected in varying concentrations of Hex-BCH and Hex-VCL. The lagoon

wastewater samples collected from the surfaces of each of the north and

south lagoons contained only 1.4 and 2.6 ng/mL of Hex-BCH. No Hex-VCL

or chlordene was detected. It is suspected much higher levels would

have been found at lower depths in the lagoons where the sludge had

settled.

As seen in Table 22, airborne concentrations ranged from 3.0 to

30.9 ng/L for Hex-BCH, 0.5 to 8.5 ng/L for Hex-VCL and from non-detected

to 0.9 ng/L for chlordene. Although the clarifiers are not aerated,

bubbling probably caused by anaerabic action was observed during the

air sampling period. These airborne concentration ranges for Hex-BCH

and Hex-VCL over the clarifiers are as high as the airborne levels

measured over the aeration basins surveys completed during the first

five surveys (I-V) (March 22-24, 1979). The airborne concentration

range for the aeration basins during these field surveys ranged from

1.4 to 27.0 ng/L for Hex-BCH and from 0.29 to 12.4 ng/L for Hex-VCL.

A very strong pesticide odor was noted during the air sampling of

the clarifiers. The workers commented that this odor over the

clarifiers was quite unusual. Nevertheless, at least on the day

sampled, the clarifiers, a non-aerated source, generated airborne con-
centrations as high as the aeration basin locations. In contrast, the
airborne levels for Hex-BCH, Hex-VCL and chlordene were quite low over
the lagoons which are non-aerated.

As seen in Table 22, side by side sampling with charcoal and
Chromosorb 102 tubes at the lagoons demonstrated that the charcoal tube
is not efficient in collecting Hex-related compounds. No Hex-BCH, Hex-
VCL or chlordene was found with the two charcoal samplers at the lagoons
whereas 0.07 and 0.7 ng/L for Hex-BCH, non-detected and 0.4 ng/L for
Hex-VCL and 0.01 and 0.3 ng/L for chlordene was found with the two
Chromosorb 102 samplers. In Section 3.3.4, the efficiency of the
Chromosorb 102 tube experiment is discussed (88 and 97% efficiencies
were determined for Hex-BCH).

3.1.6 Contact Aeration Basins Emission Rates Surveys (VII,VIII)

The mass balance approach to estimate the emission rate requires
a uniform wastewater concentration throughout the process unit at any
given time. The grab sample technique for the wastewater samples may
yield a high variability in the wastewater concentration of the Hex-
related compounds because of non-uniform distribution of each Hex-
related compound within the wastewater of the aeration basins, inlet
or outlet channels. Thus, to obtain a consistent mass balance, uni-
form wastewater concentrations within each individual aeration basin
are required to determine the emission rate.

The wastewater concentration results for the morning and after-
noon surveys (VII and VIII) of the contact aeration basins are pre-

sented in Tables 23 and 25, respectively. The wastewater concentrations were far too variable to complete a mass balance. As an example, the four initial wastewater Hex-BCH concentration in the aeration contact basins of the morning survey (Table 23) ranged from 530 to 2350 ng/mL. Similar inconsistent trends were observed for the wastewater concentration results of the Hex-VCL and chlordene . No improvement was noted with the wastewater concentration of the afternoon survey (Table 25).

The air sampling data for the morning and afternoon surveys is presented in Tables 24 and 26, respectively. In both surveys, a higher airborne concentration range was found for Hex-BCH (104.1 to 349 ng/L) than for Hex-VCL (16.7 to 72.1 ng/L) and chlordene (1.6 to 8.3 ng/L). Similarly, as seen in Tables 23 and 25, the wastewater concentration range in the aeration basin was higher for Hex-BCH (530 to 2350 ng/mL) than for Hex-VCL (250 to 765 ng/mL) and chlordene (67 to 220 ng/mL). Since there was more Hex-BCH available for stripping from the wastewater, a higher airborne level was expected.

An emission rate was calculated from the air sampling data by assuming a box model atmospheric dispersion model (See Section 1.2.6.1 for details). The results of the emission rate determination of both morning and afternoon surveys is presented in Table 27. The Hex-BCH emission rate was 3.71 g/min for the morning survey and 2.88 g/min in the afternoon survey. Similarly, the Hex-VCL emission rates were 0.75 and 0.56 g/min, respectively. The chlordene emission rate was 0.08 and 0.06 g/min, respectively. The afternoon emission rates were probably lower because the air flow through the contact aeration basins was decreased by 10%.

3.1.7 Grit-Chamber Weir Emission Rates Surveys (IX,X)

The results of the wastewater samples collected for an afternoon
and morning weir surveys are presented in Tables 28 and 30, respectively.
As with the mass balance of the contact aeration basins surveys, these
results are too variable to allow determination of an emission rate from
a mass balance. This technique for the grit-chamber weir was previously
outlined in Sections 1.2.5.2 and 3.1.6. In fact, because of high sample
variability, some of the concentration values reported in Tables 28 and
30 for the downstream positions were higher than the upstream position.
The mass balance approach assumed a decrease in wastewater concentration
from the upstream to downstream position. This difference in wastewater
concentration would have then allowed determination of an emission rate.

Air sampling data for the afternoon and morning weir surveys are
presented in Tables 29 and 31. Neither survey generated detectable
levels for Hex-BCH, Hex-VCL or chlordene with the charcoal tubes. With
the Chromosorb 102 tube, only Hex-BCH was noted as detectable levels.
Fortunately, the wind during the afternoon weir study was directly
perpendicular to the weir, which fits the atmospheric dispersion line-
source model as described in Section 1.2.5.2 without wind direction
correction. This data was analyzed with this model to calculate the
emission rate for Hex-BCH from the weir, which is summarized in Section
7.4. The average Hex-BCH emission rate from the afternoon weir survey
was 0.013 g/min. This calculated emission rate from the weir is much
less than the 2.88 and 3.71 g/min calculated emission rate for Hex-BCH
from the contact aeration basins. Based on the influent flow and

influent concentrations of Hex-BCH, this plant received 12,000 g/Day of Hex-BCH during this emission rate survey. Thus, approximately 35% of the Hex-BCH received at the plant was released from the contact aeration basins and only 0.15% from the grit-chamber weir.

The results of the morning weir survey were not analyzed with the atmospheric dispersion model, as described above because the wind direction was due north or directly along the weir line. With this wind direction, no correction can be made to the atmospheric dispersion model.

3.2 Initial Bench-Scale Aeration System Experiments   .

The initial experiments confirmed that Hex-BCH was stripped by aeration from aqueous solution by first order kinetic decay. Regardless of the type or concentration of the suspended solids, this kinetic decay pattern was still observed. The results of the four Hex-BCH experiments are summarized in Table 32 and the data plotted on Figure 16. The slope of the straight lines (Figure 16) represented the first order kinetic decay constant, which are listed in Table 32. The 5000 mg/L cellulose experiment run was extended to 12 hours and the first order decay trend was still apparent after the 12th hour of aeration. The coefficient ofcorrelation for the linear regression line (log concentration versus time) exceeded -0.978 for each of the four experiments. The double distilled water solution without suspended solids had a decay constant of -0.498 hr^{-1}. The addition of cellulose or filtercake as suspended solids to the water decreased this decay constant. For

the cellulose, an increase in the suspended solids concentration (500 to 5000 mg/L) decreased the decay constant from -0.406 to -0.228 hr^{-1}. This would imply that the stripping rate of Hex-BCH was decreased as the suspended solids level was increased.

The presence of filtercake as a suspended solid also resulted in first order decay. However, it must be pointed out that the kinetic decay constant determined for this initial experiment can not be compared directly with the cellulose experiments because the kinetic decay constant depends on the geometry of the aeration vessel (2). In the filtercake experiment, a five liter round bottom flask was used as the aeration vessel. In tne distilled water and cellulose experiments, a two liter Erlenmeyer flask was used as the aeration vessel. Also, it was observed that the initial concentration for Hex-BCH in the filter-cake wastewater (260 ng/mL) was much higher than the initial concentrations for the cellulose experiments (40 to 50 ng/mL). This could be due to the higher affinity of Hex-BCH to filtercake than to the cellulose.

The first order kinetic decay constant is directly proportional to the Henry's Law constant. This constant can be determined by:

$$H = \frac{Ka\ V\ R\ T}{G} \qquad\qquad \text{Eq. (21)}$$

where H = Henry's Law constant (atm m^3 gmole^{-1}).

Ka = First order decay constant (hr^{-1}).

V = Volume of aqueous solution in system (2 x 10^{-3}m^3).

T = Temperature (297.2^{0}K).

R = Universal Gas Constant (8.212×10^{-5} atm m^3 gmole^{-1} $^{0}K^{-1}$).

G = Aeration Rate (35 cc/min or 2.1×10^{-3} m^3 hr^{-1}).

In the initial experiments V, T, and G were kept constant. If the first-order Kinetic decay is applicable for Hex-BCH, then the Henry's Law constant can be determined with EQ. 21.

MacKay et al. (11) have also defined the Henry's Law constant as the vapor pressure of the solute (P) divided by the aqueous solubility (C) (H = P/C). However, no literature values for P or C for Hex-BCH could be located. To establish the validity of the experimental approach to determine the Henry's Law constant, H, the literature values of the vapor pressure (P) and the aqueous solubility (C) for chloroform were used (28,29).

Since the plot of the log of the $CHCl_3$ concentration data versus time yield a straight line, the slope was defined as the first-order decay constant, Ka. The Henry's Law constant for $CHCl_3$ was calculated (H = Ka V R T/G) and compared to the Henry's Law constant derived from the literature values of P = 0.21 atm and C = 68.7 gmole $CHCl_3$ per cu. meter of H_2O. The kinetic decay constant was -0.152 hr^{-1}, which corresponded to a experimentally determined Henry's Law constant of 3.55×10^{-3} m^3 atm gmole^{-1}. The calculated Henry's Law constant based on the literature values for P and C was 3.06×10^{-3} m^3 atm gmole^{-1}. The experimental value agreed quite well with the calculated values of the Henry's Law constant, which suggests confirmation of the MacKay et al. (11) experimental approach to determine the Henry's Law constant.

The values for the Henry's Law constants from the initial Hex-BCH experiments are presented in Table 32. Without the presence of suspended solids, H was determined to be 5.70×10^{-3} atm m^3 gmole^{-1}. With 500 mg/L cellulose, it was decreased to 4.73×10^{-3} atm m^3 gmole^{-1} and for a 5000 mg/L cellulose suspended solids concentration, it was decreased further to 2.65×10^{-3} atm ^{3} gmole^{-1}. This decrease in H with an increase in suspended solids concentration was expected since the Henry's Law constant was directly proportional to the kinetic decay constant. However, since Gaudy et al. (2) noted that the decay constant was depended on the physical dimensions of the aeration vessel, this experimental approach of MacKay to determine the Henry's Law constant must consider this limitation as well. Therefore, the Henry's Law constant for the filtercake experiment in the five liter round bottom flask (8.18×10^{-3} atm m^3 gmole^{-1}) can not be compared directly with the double-distilled water or the two cellulose experiments in the two liter Erlenmeyer flask.

3.3 Bench-Scale Aeration Model Experiments

The average decay constant for each of the three tested effects: aeration rate, suspended solids concentration and detergent level are presented in Table 33. The decay constant for each experiment is presented in Appendix 7.4 with a corresponding coefficient of correlation. In general, the increase in the aeration significantly increased the decay constant value for both Hex-BCH and $CHCl_3$. An increase in the suspended solids concentration drastically reduced the value of the decay constant for Hex-BCH but the value for $CHCl_3$ was only slightly

reduced. An increase in the detergent level resulted in an increased value for the Hex-BCH decay constant but no effect was noted for $CHCl_3$.

The detergent level was selected as a test parameter because oxygen transfer in aerated aqueous solution is influenced by surfactant concentration. A minimum rate of oxygen transfer was observed at a specified surfactant level (21). An increase or decrease in the surfactant concentration from this minimum value will improve the oxygen transfer. Figure 17 shows that an increase in detergent level from 0 to 40 ppm LAS detergent results in a linear increase in the mean kinetic decay constant for Hex-BCH. Thus, an increase in the detergent level enhanced stripping of Hex-BCH from the wastewater solution.

3.3.1 ANOVA Analysis

The data was analyzed by a three-way analysis of variance (ANOVA) with each of the factors assumed to be fixed (27). The concentration data appears to have a log-normal distribution. Thus, the ANOVA results (Table 34) were presented with the log_{10} of the decay constant as the response variable. For Hex-BCH, the effects of aeration rate (A), suspended solids concentration (S) and detergent level (D) were highly significant ($p < 0.0001$). However, it must be pointed out that the interactions were also significant. For chloroform, only the aeration rate factor was significant ($p < 0.0001$). For the suspended solids factor, there is slight significance ($p = 0.0984$). No interactions were significant for chloroform.

3.3.2 Laboratory Study Using Mixed Liquor from Local Activated-Sludge Plant

Since the laboratory experiments were completed with a simulated wastewater solution, a duplicate actual sludge experiment was accomplished to establish the validity of this technique. The sludge was obtained from an activated-sludge basin at the Mill Creek Sewage Treatment Plant, Cincinnati, Ohio. Chloroform and Hex-BCH were added to the sludge and stirred overnight to assure even distribution of the compounds in the wastewater system. The kinetic decay constant, K_a for Hex-BCH was -0.057 hr^{-1} with a corresponding correlation coefficient R of -0.637 for system #1 and K_a = -0.066 hr^{-1} with R = 0.721 for system #2. The kinetic decay constant for chloroform was -0.293 with R = 0.980 for system #1 and K_a = -0.263 with R = -0.991 for system #2. The suspended solids concentration of 4200 mg/L was determined in accordance with standard procedures (30). The detergent analysis was attempted, which was the standard methylene blue method (30). It failed because of a green-colored interference. These results show that the actual sludge had a much higher suspended solids concentration (4,200 mg/L) than those levels studied in the laboratory experiments (500-1500 mg/L). The higher suspended solids level of the actual sludge made uniform sampling of the wastewater difficult. Because the Hex-BCH was adsorbed onto the sludge, the non-consistent sampling of the wastewater resulted in variable Hex-BCH concentrations. Thus, the regression model for the Hex-BCH decay constant did not fit as well as with the simulated sludge experiments. Inspite of the suspended solids sampling problems, the

chloroform results were still highly linear (correlation coefficients of -0.989 and -0.991). This again confirms that chloroform was stripped without interference from the suspended solids.

3.3.3 Aeration Rate Model

Engelbrecht (1) was able tc empirically fit the first order decay constants (Ka) for butanone and acetone to the form Ka = C Q^N (Eq. 1), where C and N are empirical constants and Q is the aeration rate. Hex-BCH and $CHCl_3$ decay constants from the bench-scale aeration unit experiments were incorporated in this model (See Appendix 7-3 for a caclulator program). The C and N values (Table 35) are presented for each specific suspended solids and detergent concentration level. The Hex-BCH results show that C and N vary for each suspended solids and detergent concentration level. This was suspected prior to the aeration rate modelling analysis since the ANOVA analysis had already shown that the suspended solids and detergent concentration would influence the Hex-BCH decay constant. The aeration rate model generated similar C and N values for chloroform at all suspended solids and detergent concentration levels. This aeration rate modelling analysis would suggest that the $CHCl_3$ decay constant was independent of the suspended solids and detergent concentration level.

3.3.4 Adsorbent Tube Data

The stripping of either Hex-BCH or $CHCl_3$ from the laboratory aeration unit can be determined by the weight of the Hex-BCH and $CHCl_3$ collected on the adsorbent tube, which was placed in the off-gas exit

stream of laboratory aeration unit (Figure 15). However, this collected weight found on the adsorbent tube could not be used as a response variable for describing the stripping of Hex-BCH and $CHCl_3$ from the aqueous solutions. A change in the aeration rate altered the collection/desorption efficiency of Chromosorb 102 for Hex-BCH and $CHCl_3$. The mean collection/desorption efficiency or recovery fraction of Chromosorb 102 for Hex-BCH and $CHCl_3$ at each tested aeration rate is listed in Table 36. Many of the individual Hex-BCH experiments generated recovery fractions which exceed one. This suggests either gross contamination during sampling, extraction, storage or analysis. Because of this suspected contamination no analysis of the collected weight data from the adsorbent tubes were completed.

The data in Table 36 shows a definite trend for chloroform. As the flow rate is increased the recovery fraction dropped significantly. The mean recovery fraction at the 17.5 cc/min flow rate was 0.22 which decreased to 0.0020 at the 280 cc/min flow rate.

In the field studies, the flow rate of the air samplers was maintained between 250 to 300 cc/min. Therefore, this recovery fraction or collection/desportion efficiency of 0.0020 needs to be incorporated into the field study results for chloroform to give a more realistic estimate of the actual airborne chloroform concentration. Thus, the airborne concentrations for chloroform presented in Table 16 should be multiplied by 500 to give a better estimate of the actual chloroform concentrations.

The data in Table 36 for Hex-BCH is far too inconsistent to estimate the recovery fraction or the collection/desorption efficiency

for the field studies. The determination of the collection/desorption efficiency for Hex-BCH with the field survey air samplers (MSA Model G Air Sampler) was necessary. A known amount of Hex-BCH was injected onto a filter in a 37 mm cassette. This filter was connected to two 100 mg Chromosorb 102 tubes in series. These tubes were connected to the MSA Model G Air Sampling pump, which was calibrated to 250 cc/min flow rate. After a 10-minute run, the tubes were desorbed and analyzed in accordance with the procedure described in Appendix 7-1. A recovery fraction of 0.88 to 0.97 was found for the first tube. No Hex-BCH was found in the second adsorbent tube, indicating that breakthrough had not occurred. The range in the recovery results was probably due to technique. Because of the near quantitative recovery for Hex-BCH, no correction was made on the field survey data. Pure standards for Hex-VCL and chlordene were not available to determine their recovery fractions from Chromosorb 102. Because of similar structure and molecular weight, these compounds should have comparable Chromosorb 102 recovery fractions as that of the Hex-BCH.

3.4 Suggestions for Future Studies

A field study of an activated-sludge sewage treatment plant during a spill episode will be of great value. Aeration basin air sampling over a prolonged time period will verify the time duration of release from the aeration basins following a slug flow of a contaminant. Several conditions are required for this study, which are as follows:

i.) No prior release of the compound to the plant and then a defineu

slug of a compound received in the influent of a sewage treatment plant. ii.) A sampling and analytical method to determine the waste-water and airborne concentration of the contaminant. iii.) A method of notification to the investigator by the sewage treatment plant to allow set-up of the measuring equipment just prior or just after the slug flow has reached the plant. This notification to the investigator will, of course, depend on the fact that the sewage treatment plant management has knowledge of a pending spill (i.e., an upstream in-dustrial user has notified the plant of a spill of an industrial con-taminant). Form these conditions it is obvious that this study can not be preplanned but requires an investigator with a flexible time schedule and rapid access to sampling equipment.

Another field study to determine the emission rate of more water-soluble chlorinated hydrocarbons such as chloroform from the grit-chamber weir would validate or disprove the hypothesis of significant release of these specific compounds from this source.

Two additional parameters that could be investigated with the present laboratory system are temperature and defoaming agents. Nor-mally, sewage ranges from 60 to 80°F in the northern U.S. region year round and the study could be confined to this thermal range. It is believed that increased temperature would enhance stripping of the contaminants from the wastewater solutions. A second parameter of in-terest is defoaming agents, which are used by sewage treatment per-sonnel to suppress foaming action on the surface of the aeration basins.

These defoaming agents could influence the stripping of contaminants from the aeration basins.

Also, the laboratory studies could be completed at higher suspended solids levels. However, modifications to the present bench-scale aeration unit system are necessary to assure uniform mixing. One possibility would be a redesign of the vessel shape to a narrow rectangular channel (to simulate the actual aeration basin design) with long air diffusers at the bottom to allow rollover of the wastewater solution.

The laboratory studies could be conducted with actual sludge consisting of living biomass instead of inert simulated sludge. However, experimental runs conducted over a long period of time would not allow valid comparisons of various parameters. The living biomass changes over time and this could influence the response variables (i.e., decay constant) as much as any change in a test parameter.

The laboratory studies could be extended to test other compounds and determine their release from the wastewater solution and how various parameters such as aeration rate, suspended solids concentration, detergent level, and so on, influence that release.

4.0 DISCUSSION

The operation of an activated-sludge sewage treatment plant involves many hydraulic, physical and biological considerations. Based on the field and bench-scale aeration unit studies, certain operational procedure modifications are recommended to reduce the atmospheric exposure of hazardous compounds to the sewage treatment workers. Following receipt of a hazardous compound or compounds in the influent of the plant, the operator can consider several courses of action.

More readily water-soluble compounds such as chloroform were found to be more significantly released from the grit-chamber weir than water-insoluble compounds such as Hex-BCH. The results of this study indicated that the Hex-BCH was adsorbed onto the suspended solids whereas the chloroform was dissolved in water. Therefore, if a sewage treatment plant receives periodic slugs of more water-soluble compounds such as chloroform, covering the grit chamber weir and collection and treatment of the off-gas may significantly reduce worker exposure. However, a water-insoluble compound such as Hex-BCH, which is adsorbed onto the biomass, will be released to the atmosphere later in the plant.

It can not be assumed that following a slug flow of a hazardous chemical compound, that the worker exposure time is limited to the passage of the slug flow in the main wastewater stream through the plant. The results of the field studies suggest that after flow through the aeration basins and flow into the clarifiers, that the hazardous compounds such as Hex-BCH, Hex-VCL and chlordene, which are adsorbed on the activated-sludge, are returned to the front of the plant. The

settled sludge from the clarifiers with the adsorbed compounds is pumped back to the aeration basins. To reduce the overall time of exposure to the sewage treatment workers, the operator could reduce the return rate of sludge to the contact basins. This would decrease the suspended solids level in the contact aeration basins. Also, he or she could increase the aeration rate to further enhance stripping of the adsorbed compounds. During these procedures, the workers should wear proper respiratory equipment if their presence is required in the contact basin area. These procedures could in effect make the exposure more acute (short-termed) where worker acceptance of the respirator is more likely than a long-term low-level exposure. Once the slug of the hazardous contaminant in the influent has passed through the aeration basins, it is possible to prevent completely the atmospheric release from the aeration basins. This would require cessation of the return sludge from the clarifiers to the aeration basins. This procedure is very unlikely because it is necessary to maintain a proper biomass level in the aeration basins. If a compound is very hazardous such that it could influence the biomass survivability, it may be best to prevent the return of the sludge to the front of the plant from the clarifiers. This sludge could be collected and pumped to another treatment unit for further processing (i.e., sludge lagoon for storage or wet-oxidation process).

In the design phase of sewage treatment plants, if the design engineers perceive that a sewage treatment plant would receive periodic slugs of very hazardous materials, they should make appropriate

design considerations. One effective means but costly would be to have

holding tanks to accept receipt of the hazardous influent, to await

further and more refined treatment, such as wet-oxidation. Unfor-

tunately, most municipal sewage-treatment plants are designed for the

receipt of domestic sewage waste, which ignores the potential of highly

hazardous industrial sewage wastes. Fortunately, the U.S. Environmental

Protection Agency, has begun an aggressive program to reduce the in-

tentional release of industrial hazardous wastes to municipal sewers

but the problems of deliberate illegal dumpings will persist. The

preferred location for interception of the slug flow of contaminant

is at the producing discharger since the volume of waste involved would

be much less.

Obviously, the municipal sewage treatment plant requires knowledge

of when a hazardous slug has entered their plant. This necessitates

that the plant have an effective chemical analysis capability as well

as an effective communication system with its industrial users. If a

spill occurs, the industrial user should notify the sewage treatment

plant. Many times this has not occurred and the plant must rely on

their inplant chemical analysis. If this fails, as it does often, es-

pecially because of the inherent time delays, ' notice of the spill

comes from the sewage treatment plant workers who may complain of of-

fensive odor and/or associated occupationally-induced illness.

5.0 CONCLUSIONS

The field studies revealed that the Hex-related compounds such as Hex-BCH, Hex-VCL, and chlordene were adsorbed on the biomass and re-cycled back into the aeration basins thereby prolonging their at-mospheric release. More water-soluble compounds such as chloroform, carbon tetrachloride and tetrachloroethylene are more significantly released from the grit-chamber weir. Data from the aeration basin study suggest that the airborne concentrations for the Hex-related compounds increase in the downwind locations and that atmospheric re-lease was enhanced by increased aeration and decreased suspended solids levels.

In a separate field study, a high level of atmospheric release of Hex-related compounds was found over the clarifiers whereas the release from the sludge lagoons was quite low. A mass balance approach to estimate the release of Hex-related compounds from the contact aeration basins and grit-chamber weir failed because of large var-iations in the concentrations of the collected wastewater samples. A comparison of the Hex-BCH release from the contact aeration basins (3.71 and 2.88 g/min) and the grit-chamber weir (0.013 g/min) suggest a far more significant release from the contact aeration basins.

In the initial laboratory studies, Hex-BCH was released from sim-ulated wastewater solutions with various suspended solids concen-trations with first order kinetic decay. An increase in the suspended solids concentration decreased the stripping rate of Hex-BCH from the wastewater solution. In the laboratory experiments with the bench-

scale aeration unit, three factors (aeration rate, suspended solids concentration and detergent level) were studied. For Hex-BCH, all three factors as well as interactions were significant. For more water soluble chloroform, only the aeration rate factor was significant. The suspended solids concentration and detergent level factors did not affect the stripping of chloroform from aqueous solutions containing suspended solids.

The best procedure recommended following a slug flow of a water-insoluble hazardous material such as Hex-BCH into an activated-sludge plant appears to be as follows:

i.) Decrease the return sludge rate to the aeration basins from the clarifiers. ii.) Increase the aeration rate in the aeration basins. iii.) Have workers wear respirators in the aeration basin area during the acute exposure phase. This approach will decrease the suspended solids concentration in the aeration basin and in combination with the increased aeration enhance the stripping of the water-insoluble compound. However, workers must be protected from the acute high level exposure either by isolation or respiratory protection. On the otherhand, a more water-soluble compound such as chloroform may require plant modifications such as covers and off-gas collection over the weirs in the primary treatment areas of the sewage treatment plant.

6.0 TABLES AND FIGURES

6.1 Tables

Table 1

Summary of the Field Surveys Conducted[a]

Survey Name	Date 1979	Time of Air Sample	Weather	Average Wind Veolcity MPh	Wind Direction
Rainy Day	3/22	4PM-6PM	Showers	4-5	W
Clear Day	3/23	9AM-1PM	Cloudy	4-5	W-NW
Clear Night	3/24	6PM-10PM	Clear	0-4	W
Aeration Basins	3/24	9AM-1PM	Clear	10-15	W
Confined Space Clarifiers and Lagoons	3/22	9AM-1PM	Showers	4-5	W
Morning Aeration Basin Mass Balance	9/11	11AM-3PM	Clear	1-2	W-NW
Afternoon Aeration Basin Mass Balance	9/12	10AM-10:30	Clear	2-3	W-NW
Afternoon Grit-Chamber Mass Balance	9/12	12:30-1PM	Clear	2-3	W-NW
Morning Grit-Chamber Mass Balance	9/12	2:30-3PM	Clear	1-2	W
	9/13	7:15-7:45AM	Showers	0-1	N

a. For Surveys (1-5) the wastewater samples were collected at the midpoint of the air sampling survey. For Surveys (5-10) the wastewater samples were collected just prior to the beginning of the air sampling survey and again just after completion of the survey.

Table 2

Parameters of the Various Aeration Basin Types
at the North Sewage Treatment Plant, Memphis, Tn.
for the Dates of the Field Surveys[a]

| | Suspended Solids, mg/L[b] | | | Air Flow Rate, KCFM[c] | | |
| | contact[d] | stab. | digester | contact | stab.[d] | digester |
Date	mg/L	mg/L	mg/L	KCFM	KCFM	KCFM
3/22/79	3,900	15,000	11,600	93	86	32
3/23/79	3,800	14,000	12,000	91	101	32
3/24/79	4,400	13,000	12,300	91	100	31
9/11/79	7,600	16,000	14,000	136	80	58
9/12/79	8,200	15,000	13,000	184	41	61
9/13/79	8,000	16,000	14,000	140	41	56

a. The data was provided by Mr. Joe Taylor, plant manager, North
    Sewage Treatment Plant, Memphis, Tn.

b. The wastewater samples were collected at 6:00AM.

c. The air flow rates are reported as KCFM, 1000 cubic
    feet per minute at an average temperature of 149°F
    (range 131-161°F) and at an average pressure of 7.3
    psig (range 7.1-7.5 psig).

d. Stab. refers to the Stabilization Basins.

Table 3

Summary of Initial Experiments Conducted

Suspended Solids (SS) Type	SS Concentration mg/L	Reaction Vessel	Liquid Volume,L
1. Double Distilled Water (DDW)	0	Two Liter Erlenmeyer Flask	1.0
2. Cellulose	500	Same as DDW	1.0
3. Cellulose	5000	Same as DDW	1.0
4. Filtercake	500	Five Liter Round Bottom Flask	2.5

Table 4

Summary of Bench-Scale Aeration Unit Experiments

Factor	Level	Normal Operating Level Activated-Sludge Plant
Aeration Rate	17.5;35;70;140;280 cc/min	70 cc/min (a)
Suspended Solids	500;1,000;1,500 mg/L	1000-1500 mg/L (a)
Detergent Level	0;20;40 ppm	10-15 ppm (b)

(a) Metcalf and Eddy, Wastewater Engineering, McGraw-Hill, New York, New York, pp. 496-498, 1972 (30).

(b) ⌐ ⌐, T.R. and R. L. Meserve, Water and Its Impurities, 2nd edition, Dowdwn, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania, p. 274, 1974 (31).

Table 5

Wastewater Concentrations of Several Chlorinated Organic Compounds
the North Sewage Treatment Plant, Memphis, Tn.
(July 24, 1978 to August 23, 1978)[a]

Concentration, ng/mL[b]

Location	Hex-BCH		Hex-VCL		Chlordene	
	Mean	Range	Mean	Range	Mean	Range
Plant Influent	450	92-1,540	99	27-710	197	21-1,200
Digested Sludge[c]	6140	390-61,100	1280	72-14,000	2660	127-26,800
Plant Effluent	60	13-301	9	0-32	15	0-63

a. Data furnished by A. Pendergrass, Chemist, North Sewage
   Treatment Plant, Memphis, Tn. (32).

b. Daily Grab Samples were collected at 7:00 AM and no samples were
   taken on the weekends.

c. Digested Sludge was removed from the sludge lagoon influent
   after it was thickened.

Table 6

Concentrations of Test Compounds in Wastewater at the North Sewage
Treatment Plant, Memphis, Tn.
(March 22 to March 24, 1979)

Concentration, ng/mL[a]

Location	Hex-BCH		Hex-VCL		Chlordene	
	Mean	Range	Mean	Range	Mean	Range
Plant Influent	37	21-79	15	8-27	229	37-821
Digestion Basin	449	375-590	385	329-473	3930	2640-7540
Plant Effluent	6	N/D-16	3	2-3	78	47-137

a. The mean is based on five samples collected from March
   22 to March 24, 1979.

N/D refers to none detected.

Table 7

Wastewater Concentration of Plant Influent of
Several Chlorinated Organic Compounds
(March 22 to March 24, 1979)

Date	Time	Influent Flow $L \times 10^8$/day	Concentration, ng/mL		
			Hex-BCH	Hex-VCL	Chlordene
3/22/79	1:00 PM	4.25	79	27	157
3/22/79	7:00 PM	4.33	26	8	821
3/23/79	11:00 AM	4.62	26	16	63
3/24/79	11:00 AM	3.42	21	10	37
3/24/79	8:00 PM	3.62	31	15	71

Table 8

Comparison of Adjacent Wastewater and Air
Sample Results of Field Surveys (I-V)
(March 22 to 24, 1979)

Sample Number and Location	Date of Sample 1979	Time[a]	Concentration					
			Hex-BCH		Hex-VCL		Chlordene	
			WW(b) ng/mL	Air ng/L	WW(b) ng/mL	Air ng/L	WW(b) ng/ml	Air ng/L
1. Grit-Chamber[c]	3/22	4PM-6PM	28	N/D	6	0.03	100	0.2
2. Grit-Chamber[c]	3/23	9AM-1PM	22	2.4	10	0.5	57	3.3
3. Grit-Chamber[d]	3/24	6PM-10PM	49	5.0	25	1.0	180	1.3
4. Contact Basin[e]	3/23	9AM-1PM	125	11.3	91	3.0	2800	25.4
5. Contact Basin[e]	3/24	6PM-10PM	86	10.3	58	2.8	1600	21.3
6. Digester[f]	3/22	4PM-6PM	440	21.7	390	6.7	3200	26.1

a. The wastewater samples were collected at the midpoint of the air sampling survey.
b. WW refers to the wastewater concentration.
c. The air sample was collected at the Grit-Chamber Dragout, which is 50 feet from the wastewater sampling location.
d. The air sample was collected at the Grit-Chamber Weir, immediately adjacent the wastewater sampling location.
e. The air sample was collected at the center of the Aeration Basins.
f. The air sample was collected at the far north end of the Aeration Basins.

Table 9

Wastewater Sample Results of the
Rainy Day Field Survey (I)
(March 22, 1979-7:00 PM)

Sampling Number and Location	Wastewater Concentration, ng/mL		
	Hex-BCH	Hex-VCL	Chlordene
1. Wet-Well	26	8	820
2. Grit-Chamber Effluent	28	6	101
3. Lagoon Effluent	640	530	4800
4. Digester (A-15)	440	390	3200
5. Digester (B-15)	307	270	2100
6. Final Effluent	N/D	3	65

Table 10

Air Sample Results of the
Rainy Day Field Survey (I)
(March 22, 1979 4:00PM-6:00PM)

Sampling Number and Location	Air Concentration, ng/L		
	Hex-BCH	Hex-VCL	Chlordene
1. Grit-Chamber Dragout	N/D	0.03	0.2
2. North End of Aeration Basin	21.7	6.7	26.1
3. Center of Aeration Basin	18.2	12.4	52.8
4. North End of South Lagoon	0.3	0.1	0.8
5. East End of Aeration Basin	3.6	0.7	7.9
6. North End of North Lagoon	0.3	0.2	0.9

Table 11

Wastewater Sample Results of the
Clear Day Field Survey (II)
(March 23, 1979-11:00AM)

Sampling Number and Location	Wastewater Concentration, ng/mL		
	Hex-BCH	Hex-VCL	Chlordene
1. Wet-Well	26	15	63
2. Grit-Chamber Effluent	22	10	57
3. Contact Basin (A-1)	120	91	2900
4. Stab. Basin (A-7)[a]	300	230	6500
5. Digester (A-13)	400	340	2900
6. Final Effluent	16	3	88

a. Stab. Basin (A-&) refers to the Stabilization Basin of
    Battery A, Cell # 7.

Table 12

Air Sample Results of the
Clear Day Field Survev (II)
(March 23, 1979 9:00-1:00PM)

Sampling Number and Location	Airborne Concentration, ng/L		
	Hex-BCH	Hex-VCL	Chlordene
1. Top of Blowerhouse (NW)	0.3	0.08	0.3
2. Top of Blowerhours (SE)	0.1	0.04	0.2
3. Center of Aeration Basin	11.3	3.0	25.4
4. E. End of Aeration Basin	9.6	2.7	20.7
5. Grit-Chamber Dragout	2.4	0.5	3.3
6. Wet-Well[a]	6.8	2.8	11.1

a. Air sample at the Wet-Well was adjacent the dumpster, which
    collects the cparse material removed from the bar screens.

Table 13

Wastewater Sample Results of the
Clear Night Field Survey (III)
(March 24, 1979-8:00PM)

Sampling Number and Location	Wastewater Concentration, ng/mL		
	Hex-BCH	Hex-VCL	Chlordene
1. Wet-Well	31	15	71
2. Grit-Chamber Effluent	49	25	180
3. Digester (B-13)	405	380	7500
4. Stab. Basin (B-7)[a]	260	200	5100
5. Contact Basin (B-2)	86	58	1600
6. Final Efflu t	11	3	47

a. Stab. Basin (B-7) refers to the Stabilization Basin of
   Battery B, Cell # 7.

Table 14

Air Sample Results of the
Clear Night Survey (III)
(March 24, 1979 6:00PM-10:00PM)

Sample Number and Location	Airborne Concentration, ng/L		
	Hex-BCH	Hex-VCL	Chlordene
1. Grit-Chamber Weir	5.0	1.0	1.3
2. Grit-Chamber Dragout	2.5	0.7	1.8
3. W. End of Aeration Basin	3.6	0.9	5.9
4. Center of Aeration Basin	10.6	2.8	21.3
5. E. End of Aeration Basin	18.7	4.8	35.4

Table 15

Wastewater Sample Results of the Clear Night Field Survey (III)
for Chloroform (CHCl3), Carbon Tetrachloride (CCl4) and
Tetrachlorethylene (TCE)

Sampling Number and Location	Wastewater Concentration, ng/mL		
	$CHCl_3$	CCl_4	TCE
1. Wet-Well	19	160	7
2. Grit-Chamber Effluent	15	140	9
3. Contact Basin	1	6	3
4. Stabilization Basin	2	5	2
5. Digester	5	4	2
6. Final Effluent	4	1	11

Table 16

Air Sample Results of the Clear Night Field Survey (III)
for Chloroform (CHCl3), Carbon Tetrachloride (CCl4)
Tetrachloroethylene (TCE)

Sampling Number and Location	Airborne Concentration, ng/L		
	$CHCl_3$	CCl_4	TCE
1. Grit-Chamber Weir	18.9	227.1	24.3
2. Grit-Chamber Dragout	15.4	43.6	4.7
3. W. End of Aeration Basin	0.2	9.0	1.6
4. Center of Aeration Basin	0.5	27.0	5.4
5. E. End of Aeration Basin	2.6	117.7	9.6

Table 17

Wastewater Sample Results of Aeration Basin
Survey (IV) (March 24, 1979-11:00PM)

| Location | Wastewater Concentration, ng/mL | | |
	Hex-BCH	Hex-VCL	Chlordene
Plant Influent	21	10	37
Contact Basin[a]	132	97	4600
Stabilization Basin[a]	280	220	6080
Digester[a]	430	380	4020
Plant Effluent	N/D	2	54

a. The aeration basin concentration is based on the average
of two wastewater samples.

N/D refers to None Detected

Table 18

Air Sample Results of Aeration Basin
Survey (IV) (March 24, 1979 9AM-1PM)

| | Concentration, ng/L | | | | | |
| | Hex-BCH | | Hex-VCL | | Chlordene | |
Aeration Basin	Upwind	Downwind	Upwind	Downwind	Upwind	Downwind
Contact	1.4	27.0	0.3	6.8	2.2	53.0
Stabilization	1.8	16.0	0.5	3.8	3.1	37.1
Digester	0.6	6.4	0.1	2.0	0.5	7.7

Table 19

Wastewater Sample Results of the
Confined Space Field Survey (V)
(March 22, 1979-1:00PM)

Sampling Number and Location	Wastewater Concentration, ng/mL		
	Hex-BCH	Hex-VCL	Chlordene
1. Wet-Well	79	27	157
2. Grit-Chamber Effluent	89	42	174
3. Lagoon Influent	625	556	4410
4. Digester (A-15)[a]	555	452	3020
5. Digester (B-15)[b]	627	493	3720
6. Final Effluent	6	2	137

a. (A-15) refers to Battery A, Cell # 15 of the Aeration Basins as described in Figure 4.

b. (B-15) refers to Battery B. Cell # 15 of the Aeration Basins as described in Figure 4.

Table 20

Air Sample Results of the
Confined Space Field Survey (V)
(March 22, 1979-11:00AM-3:00PM)

Sampling Number and Location	Airborne Concentration, ng/L		
	Hex-BCH	Hex-VCL	Chlordene
1. East Pipe Galley	11.4	3.9	21.1
2. Central Pipe Galley	6.1	1.8	12.5
3. West Pipe Galley	2.4	0.7	3.0
4. Wet-Well	1.6	0.5	1.7
5. Air-Intake[a]	1.3	0.3	0.6
6. Control Room[b]	1.3	0.2	0.5
7. Blank	N/D	N/D	N/D

a. This air sample was collected at the air intake of the administrative and maintenance building.

b. This air sample was collected at the ventilation duct grille of the plant operations control room, which is in the administrative and maintenance building.

N/D refers to None Detected.

Table 21

Wastewater Sample Results of the
Clarifiers and Lagoons Field Survey (VI)
(Sept. 11, 1979-1:00PM)

Sampling Number and Location	Wastewater Concentration, ng/mL Hex-BCH	Hex-VCL	Chlordene
1. NE Clarifier	45	14	N/D
2. NW Clarifier	6700	220	N/D
3. SE Clarifier	7200	500	N/D
4. SW Clarifier	200	145	54
5. N Center Clarifier	125	53	14
6. S Center Clarifier	34	10	7
7. N Lagoon	3	N/D	N/D
8. S Lagoon	1	N/D	N/D

N/D refers to None Detected.

Table 22

Air Sample Results of the
Clarifiers and Lagoons Field Survey (VI)
(Sept. 11, 1979 11:00AM-3:00PM)

Sampling Number and Location	Tube[a] Type	Airborne Concentration, ng/L Hex-BCH	Hex-VCL	Chlordene
1. NE Clarifier	C102	4.6	1.6	0.1
2. NW Clarifier	C102	5.2	1.3	0.01
3. SE Clarifier	C102	30.9	8.5	0.9
4. SW Clarifier	C102	12.3	2.9	0.3
5. N Center Clarifier	C102	3.0	0.5	N/D
6. S Center Clarifier	Char	14.1	1.4	N/D
7. N Lagoon	C102	0.07	N/D	0.01
8. S Lagoon	C102	0.7	0.4	0.3
9 N Lagoon	Char	N/D	N/D	N/D
10. S Lagoon	Char	N/D	N/D	N/D

a. C102 refers to an adsorbent tube of Chromosorb 102 and Char refers to an adsorbent tube of Activated Charcoal.

N/D refers to None Detected.

Table 23

Wastewater Sample Results of the Morning
Aeration Basins Emission Rate Survey (VII)
(Sept. 12, 1979 10:00AM and 10:30AM)

Sampling Number and Location	Time of Sample	Wastewater Concentration, ng/mL Hex-BCH	Hex-VCL	Chlordene
1. N Inlet	10:00	1860	950	290
2. S Inlet	10:00	1420	690	200
3. SE Contact Basin	10:00	2350	1280	560
4. NE Contact Basin	10:00	530	250	67
5. NW Contact Basin	10:00	850	400	110
6. SW Contact Basin	10:00	825	400	115
7. N Outlet	10:00	720	350	104
8. S Outlet	10:00	900	401	110
1. N Inlet	10:30	2120	1025	340
2. S Inlet	10:30	1150	565	160
3. SE Contact Basin	10:30	1600	765	220
4. NE Contact Basin	10:30	740	360	96
5. NW Contact Basin	10:30	630	280	84
6. SW Contact Basin	10:30	1100	550	165
7. N Outlet	10:30	570	255	66
8. S Outlet	10:30	755	360	98

Table 24

Air Sample Results of the Morning
Aeration Basins Emission Rate Survey (VII)
(Sept. 12, 1979 10:00AM-10:30AM)

Sampling Number and Location	Airborne Concentration, ng/L Hex-BCH	Hex-VCL	Chlordene
1. SE Contact Basin	104.1	16.7	1.6
2. NE Contact Basin	340.4	71.9	7.9
3. NW Contact Basin	265.7	52.3	5.6
4. SW Contact Basin	349.0	72.1	8.3

Table 25

Wastewater Sample Results of the Afternoon
Aeration Basins Emission Rate Survey (VIII)
(Sept. 12, 1979 2:30PM and 3:00PM)

Sampling Number and Location	Time of Sample	Wastewater Concentration, ng/mL		
		Hex-BCH	Hex-VCL	Chlordene
1. N Inlet	2:30	1060	510	140
2. S Inlet	2:30	1200	610	175
3. NE Contact Basin	2:30	850	370	97
4. NW Contact Basin	2:30	620	290	78
5. SW Contact Basin	2:30	1080	540	150
6. SE Contact Basin	2:30	7 0	390	88
7. N Outlet	2:30	490	210	52
8. S Outlet	2:30	1200	590	175
1. N Inlet	3:00	790	370	96
2. S Inlet	3:00	1500	785	130
3. NE Contact Basin	3:00	710	310	77
4. NW Contact Basin	3:00	590	270	67
5. SW Contact Basin	3:00	660	310	84
6. SE Contact Basin	3:00	640	300	84
7. N Outlet	3:00	440	190	52
8. S Outlet	3:00	570	260	72

Table 26

Air Sample Results of the Afternoon
Aeration Basins Emission Rate Survey (VIII)
(Sept. 12, 1979 2:30PM-3:00PM)

Sampling Number and Location	Airborne Concentration, ng/L		
	Hex-BCH	Hex-VCL	Chlordene
1. NE Contact Basin	210.7	40.8	4.4
2. NW Contact Basin	277.0	54.9	5.8
3. SW Contact Basin	189.9	35.2	3.9
4. SE Contact Basin	222.0	42.2	4.4

Table 27

Contact Basin Emission Rate Calculation
Based on Air Sampling Data

Morning Survey

Position Number	Volume of Collected Air, L	Total Weight of Contaminant, ng Hex-BCH	Hex-VCL	Chlordene
1.	11.4	1188	190	18
2.	12.1	4102	867	95
3.	11.2	2969	584	62
4.	9.7	3410	705	81
Total	44.4	11669	2346	256
Emission Rate, Wc, g/min.		3.71^a	0.75	0.08

a. The Emission Rate was calculated as follows:

$$Wc = \frac{\text{Total Weight of Contaminant} \times Q}{\text{Total Volume of Collected Air}}$$

$$Wc = 11669 \text{ ng} \times 10^{-9} \frac{g}{ng} \times 1.41 \times 10^7 \text{ LPM} \times \frac{1}{44.4 \text{ L}}$$

Wc = 3.71 g/min. Hex-BCH Emission Rate from Contact Basins.

Afternoon Survey

Position Number	Volume of Collected Air, L	Total Weight of Contaminant, ng Hex-BCH	Hex-VCL	Chlordene
1.	12.8	2699	523	56
2.	11.3	3133	621	65
3.	10.6	2015	374	41
4.	10.0	2225	423	44
Total	44.7	10072	1941	206
Emission Rate, Wc, g/min.		2.88^b	0.56	0.06

b. $Wc = 10072 \text{ ng} \times 10^{-9} \frac{g}{ng} \times 1.28 \times 10^7 \text{ LPM} \times \frac{1}{44.7 \text{ L}}$

Wc = 2.88 g/min. Hex-BCH Emission Rate from Contact Basins.

Table 28

Wastewater Sample Results of the Afternoon
Emission Rate Weir Survey (IX)
(Sept. 12, 1979 12:30PM and 1:00PM)

Sampling Number and Location	Time of Sample	Wastewater Concentration, ng/mL		
		Hex-BCH	Hex-VCL	Chlordene
1. N Upstream[a]	12:30	206	59	15
2. N Downstream	12:30	238	69	15
3. S Upstream	12:30	867	94	15
4. S Downstream	12:30	300	87	20
1. N Upstream	1:00	313	85	20
2. N Downstream	1:00	337	99	24
3. S Updownstream	1:00	396	121	32
4. S Upstream	1:00	381	111	26

a. N Upstream refers to the North Upstream Sampling Position
of the Grit-Chamber Weir.

Table 29

Air Sample Results of the Afternoon
Emission Rate Weir Survey (IX)
(Sept. 12, 1979 12:30PM-1:00PM)

Sampling Number and Location	Type of Tube	Airborne Concentration, ng/L		
		Hex-BCH	Hex-VCL	Chlordene
1. 8.92 m East[a]	C102[b]	2.7	0.3	N/D[c]
2. 10.0 m East	C102	1.6	N/D	N/D
3. 15.0 m East	C102	1.2	N/D	N/D
1. 8.92 m East	Char[d]	N/D	N/D	N/D
2. 10.0 m East	Char	N/D	N/D	N/D
3. 15.0 m East	Char	N/D	N/D	N/D

a. Air Sampling Position was 8.92 m east of the grit-chamber weir.
b. C102 refers to a Chromosorb 102 adsorbent tube.
c. N/D refers to none detected.
d. Char refers to a charcoal adsorbent tube.

Table 30

Wastewater Sample Results of the Morning
Emission Rate Weir Survey (X)
(Sept. 13, 1979 7:15AM and 7:45AM)

Sampling Number and Location	Time of Sample	Wastewater Concentration, ng/mL		
		Hex-BCH	Hex-VCL	Chlordene
1. N Upstream	7:15	221	89	21
2. N Downstream	7:15	246	100	32
3. S Upstream	7:15	329	136	34
4. S Downstream	7:15	240	99	25
1. N Upstream	7:45	319	138	37
2. N Downstream	7:45	306	136	41
3. S Upstream	7:45	256	108	27
4. S Downstream	7:45	421	182	43
Blank		3	N/D	N/D

Table 31

Air Sample Results of the Morning
Emission Rate Weir Survey (X)
(Sept. 13, 1979 7:15-7:45AM)

Sampling Number and Location	Type of Tube	Airborne Concentration, ng/L		
		Hex-BCH	Hex-VCL	Chlordene
1. 8.92 m East[a]	C102[b]	1.2	N/D[c]	N/D
2. 10.0 m East	C102	1.3	N/D	N/D
3. 15.0 m East	C102	0.8	N/D	N/D
1. 8.92 m East	Char[d]	N/D	N/D	N/D
2. 10.0 m East	Char	N/D	N/D	N/D
3. 15.0 m East	Char	N/D	N/D	N/D

a. Air Sampling Position was 8.92 m East of the Grit-Chamber Weir.
b. C102 refers to a Chromosorb 102 adsorbent tube.
c. N/D refers to none detected.
d. Char refers to a Charcoal adsorbent tube.

Table 32

Kinetic Decay for Henry's Law Constants
for the Initial Hex-BCH Experiments

Suspended Solids (SS) Type	SS Con- centration mg/L	Reaction Vessel	Liquid Volume L	Decay Constant	R^a	Henry's Law Constant $H \times 10^3$ [b]
Double Distilled Water (DDW)	0.0	Two liter Erlenmeyer Flask	1.0	-0.498	-0.992	5.70
Cellulose	500.0	Same as DDW	1.0	-0.406	-0.978	4.73
Cellulose	5000.0	Same as DDW	1.0	-0.228	-0.996	2.66
Filtercake	500.0	Five liter Round Bottom Flask	2.5	-0.281	-0.978	8.18

a. R refers to the Correlation Coefficient of the linear regression line (log Wastewater Concentration verses Time).
b. Henry's Law Constant, H has units of atm m^3/ gmole.
c. These experiments were conducted at 24.6°C with an aeration rate of 35 cc/min.

Table 33

Decay Constants for Hex-BCH and $CHCl_3$ at each Specific
Level of Aeration Rate, Suspended Solids Concentration
and Detergent Level

Factor	Level	Average[a] Hex-BCH$_3$ Ka x 10^3 hr^{-1}	Average[a] CHCl$_3$ Ka x 10^3 hr^{-1}
Aeration Rate, cc/min................	17.5	46	82
	35	65	176
	70	82	308
	140	155	532
	280	249	1021
Suspended Solids Concentration, mg/L	500	139	445
	1000	103	445
	1500	78	415
Detergent Level, ppm	0	86	434
	20	115	431
	40	156	440

a. The average decay constant (Ka x 10^3) was determined from all
    experiments completed at each specified level of the three
    factors: aeration rate, suspended solids concentration and
    detergent level.

Table 34

Summary of Analysis of Influence of Aeration Rate, Suspended Solids and Detergent
Level on Hex-BCH and Chloroform Stripping*

Response Variable: $\log_{10}$ Decay Constant ($\log_{10}$Ka)

		Hex-BCH			Chloroform		
Source	DF	ANOVA SS	F Value	Pr F	ANOVA SS	F Value	Pr F
A	4	7.07	173	0.0001	14.56	250.4	0.0001
S	2	1.49	73.2	0.0001	0.07	2.4	0.0984
D	2	0.64	31.6	0.0001	0.01	0.5	0.6008
A & S	8	0.29	3.6	0.0028	0.10	0.8	0.5621
A & D	8	1.03	12.6	0.0001	0.12	1.0	0.4389
S & D	4	0.11	2.8	0.0361	0.07	1.2	0.3231
A & S & D	16	0.40	2.5	0.0078	0.22	1.0	0.5213

* Statistical Analysis by 3-way ANOVA with fixed effects (33).

Table 35

Engelbrecht Aeration Rate Model Results

S^a mg/L	D^b ppm	Hex-BCH			Chloroform		
		C^c	N^d	R^e	C^c	N^d	R^e
500	0.0	3.9	0.80	0.959	5.9	0.93	0.992
1000	0.0	4.0	0.64	0.874	7.2	0.89	0.987
1500	0.0	8.1	0.44	0.734	8.0	0.85	0.988
500	20.0	19.2	0.46	0.889	6.0	0.92	0.992
1000	20.0	17.3	0.43	0.883	7.5	0.88	0.982
1500	20.0	6.9	0.53	0.771	5.1	0.95	0.989
500	40.0	3.9	0.83	0.935	5.3	0.95	0.978
1000	40.0	6.9	0.67	0.970	7.2	0.88	0.993
1500	40.0	0.9	1.01	0.948	6.0	0.92	0.994

a. S refers to the suspended solids concentration.
b. D refers to the detergent level.
c. C refers to the empirical constant of the Engelbrecht aeration model ($Ka = C\ Q^N$).
d. N refers to the empirical exponent of the model.
e. R refers to the correlation coefficient.

Table 36

Collection/Desorption Efficiency of Hex-BCH
and Chloroform on Chromosorb 102[a] as a
Function of Aeration Rate

Flow Rate, cc/min	Hex-BCH			Chloroform		
	Recovery Fraction			Recovery Fraction		
	Mean	Std. Der.	C.V. %	Mean	Std. Der.	C.V.%
17.5	0.87[e]	2.40	280	0.22	0.11	50
35	0.37	0.20	55	0.10	0.05	50
70	0.86[e]	0.59	69	0.05	0.02	40
140	0.97[e]	0.58	60	0.01	0.003	34
280	1.28[e]	0.45	35	0.002	0.002	104

a. The Chromosorb 102 adsorbent tube consisted of 100 mg of
    collection media (80/100 mesh).
b. Recovery Fraction is the same as Collection/Desorption
    Efficiency. This recovery fraction is a mean value of 18
    experiments, which were completed at each aeration rate.
c. Std. Der. refers to the Standard Deviation.
d. C.V. % refers to the Coefficient of Variation.
e. Many of the individual experiments, which are represented
    by this mean recovery fraction had recovery fractions which
    exceed one. This would suggest gross contamination of the
    adsorbent tube during Sampling and/or analysis.
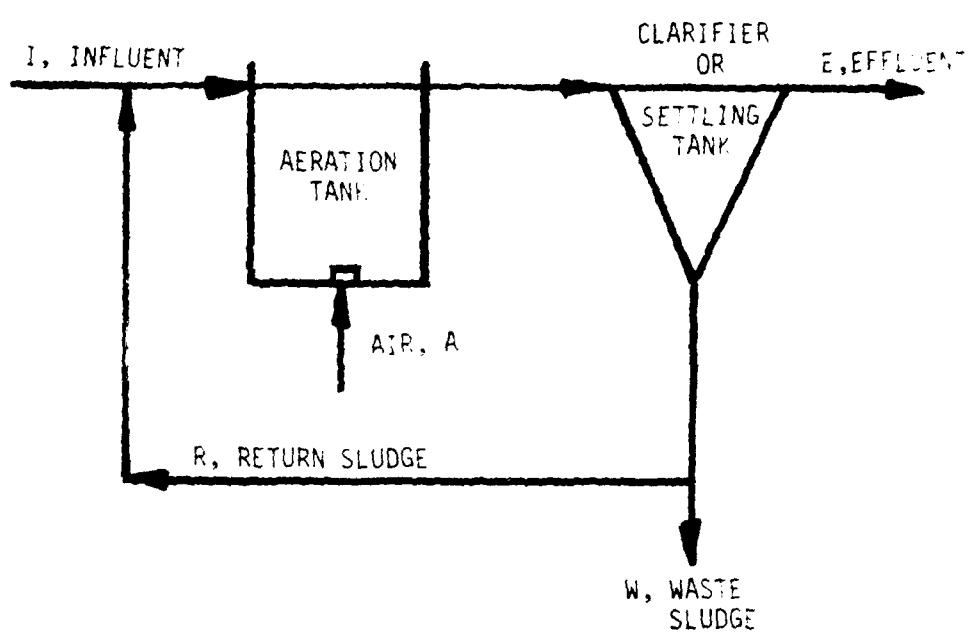
Figure 1. Conventional Activated-Sludge System
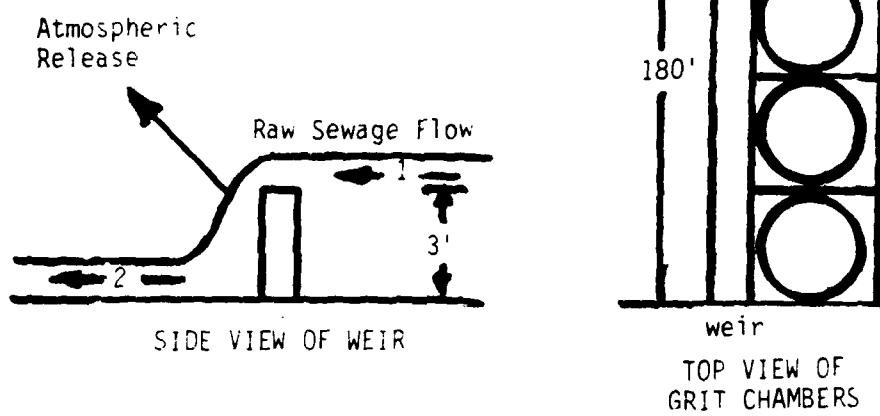
Figure 2.   Grit-Chamber Weir
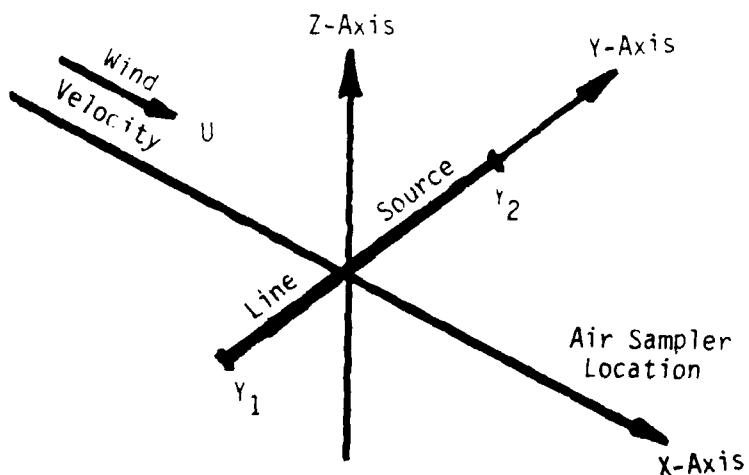
Figure 3.   Line Source Atmospheric Model
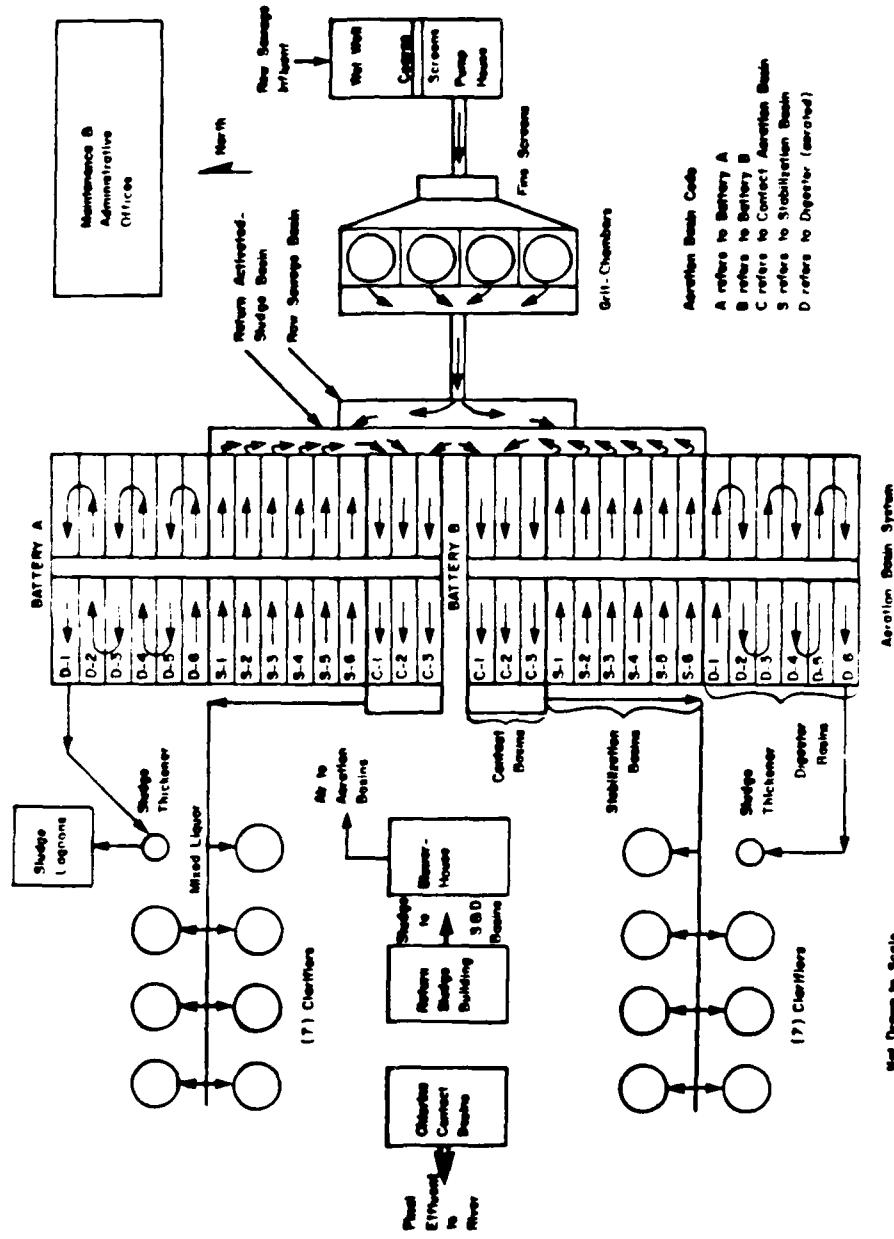
Figure 4. Physical Layout of the Plant
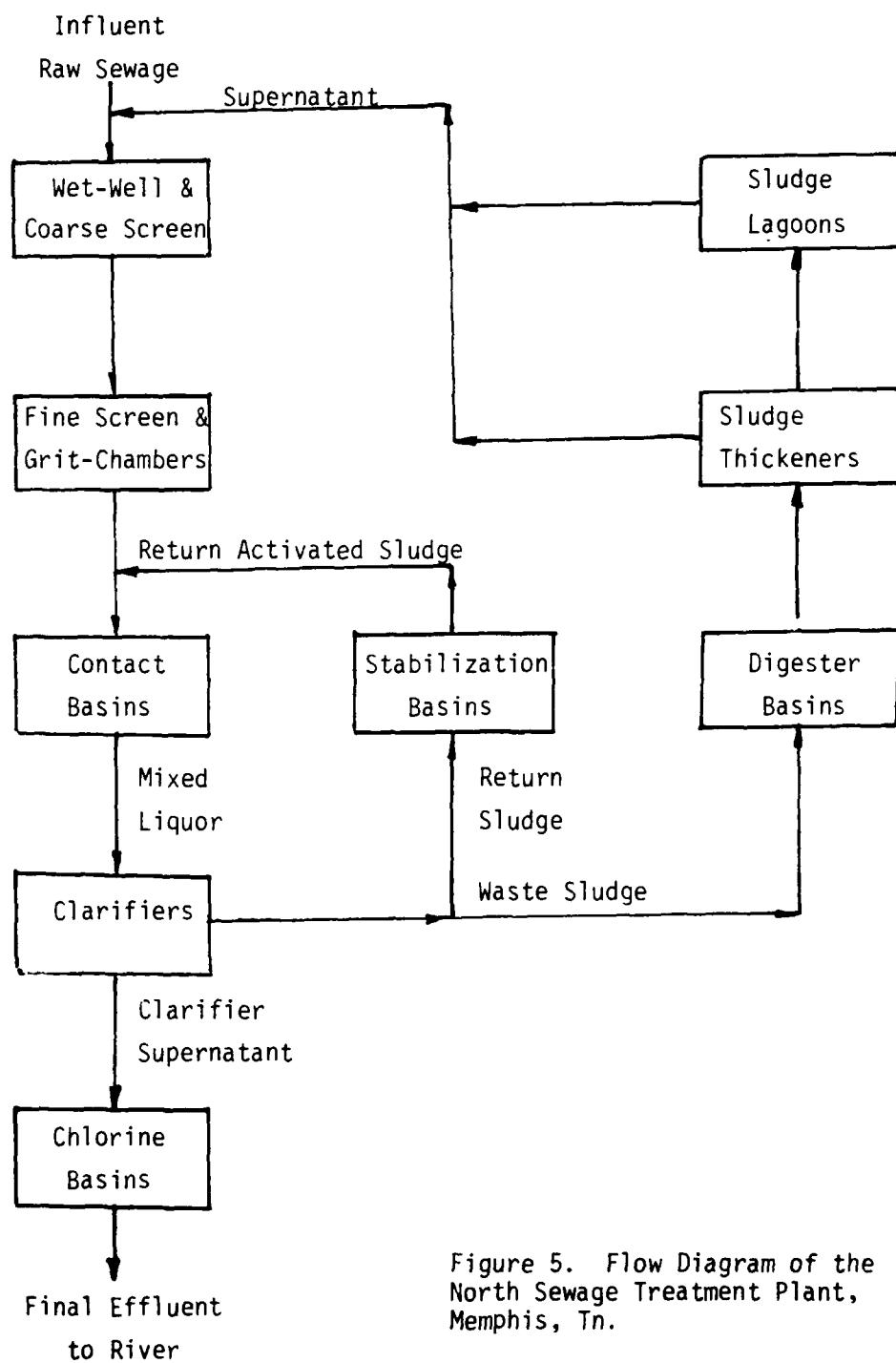
Figure 5. Flow Diagram of the North Sewage Treatment Plant, Memphis, Tn.
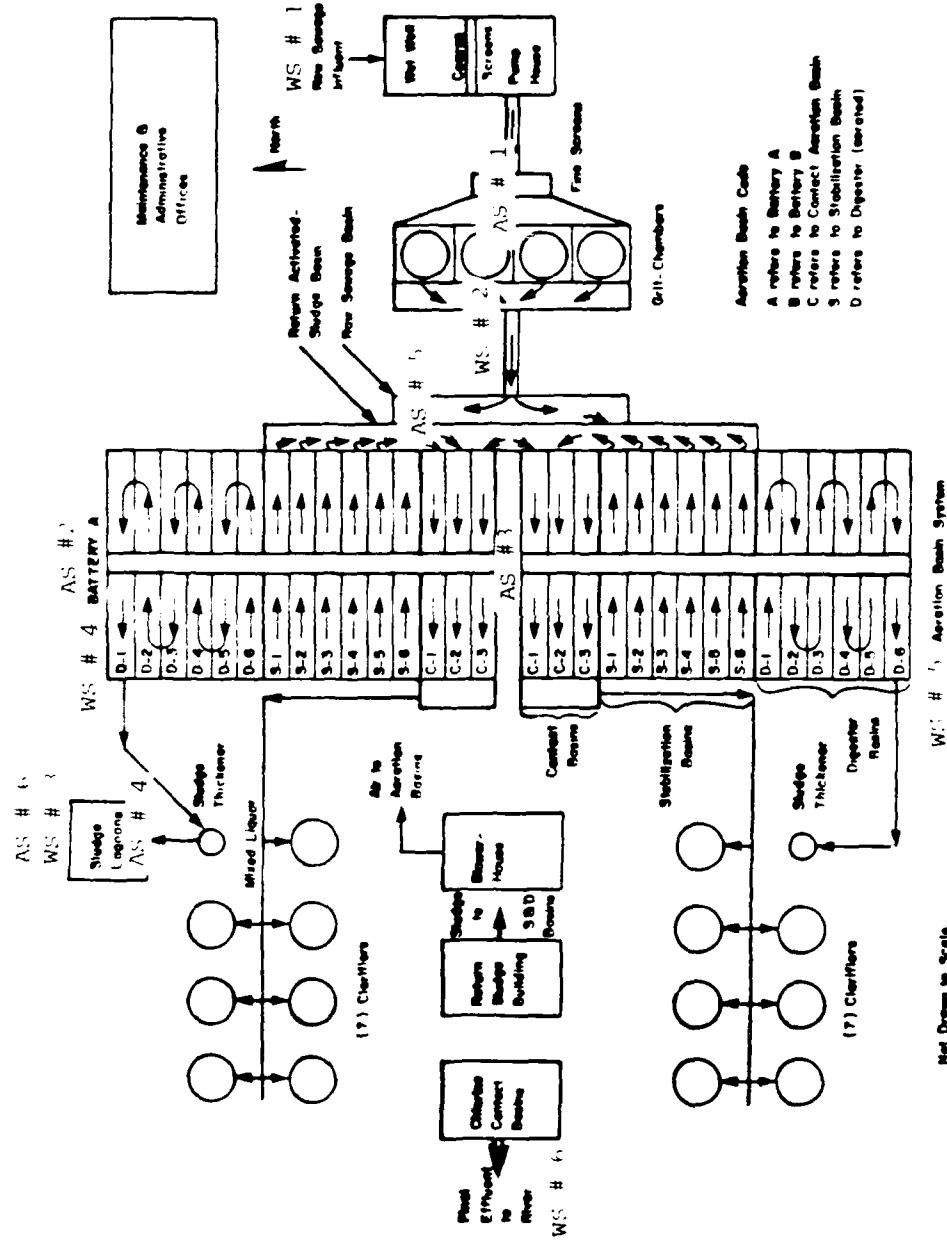
Figure 6.   Locations of Air and Wastewater
            Sampling Positions for Rainy
            Day Survey (I)
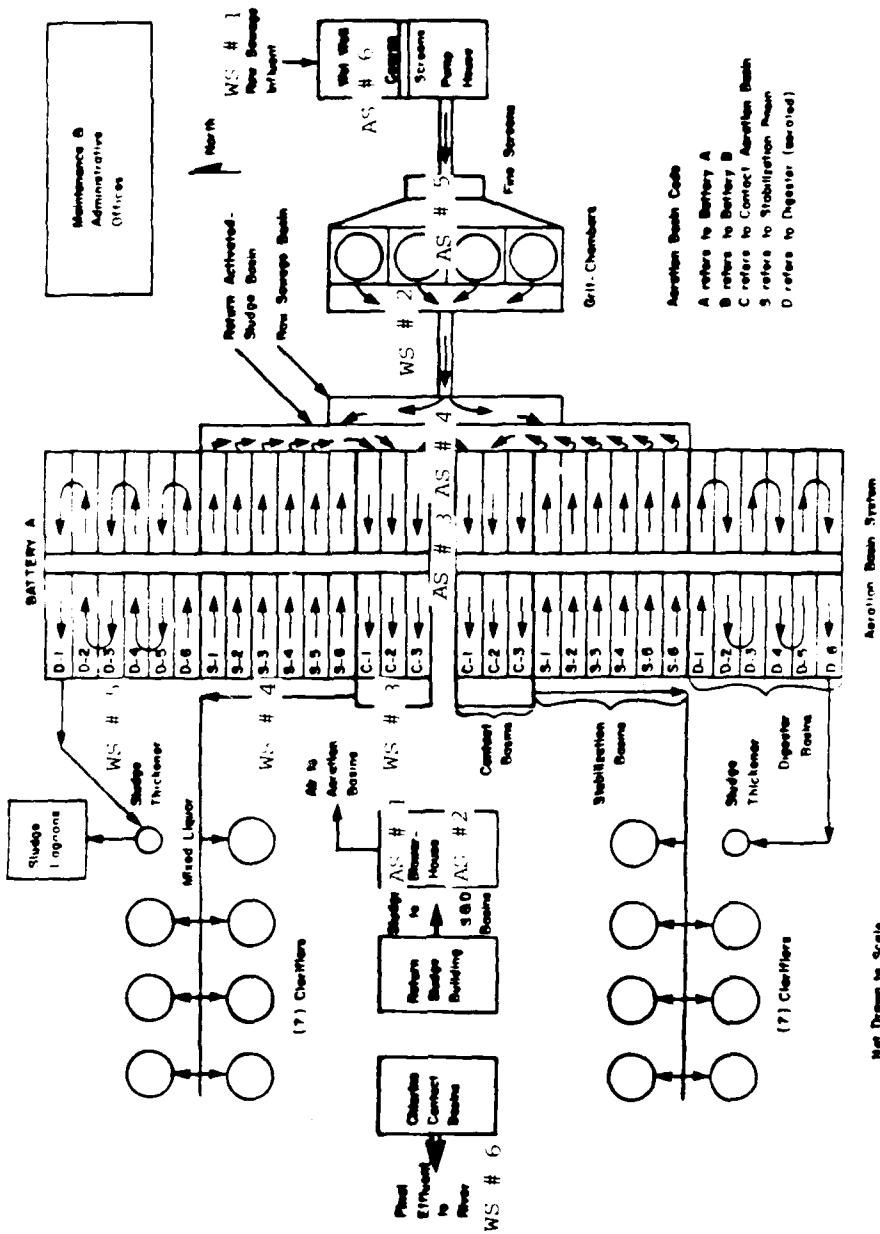
Figure 7.   Locations of Air and Wastewater
Sampling Positions for Clear
Day Survey (II)
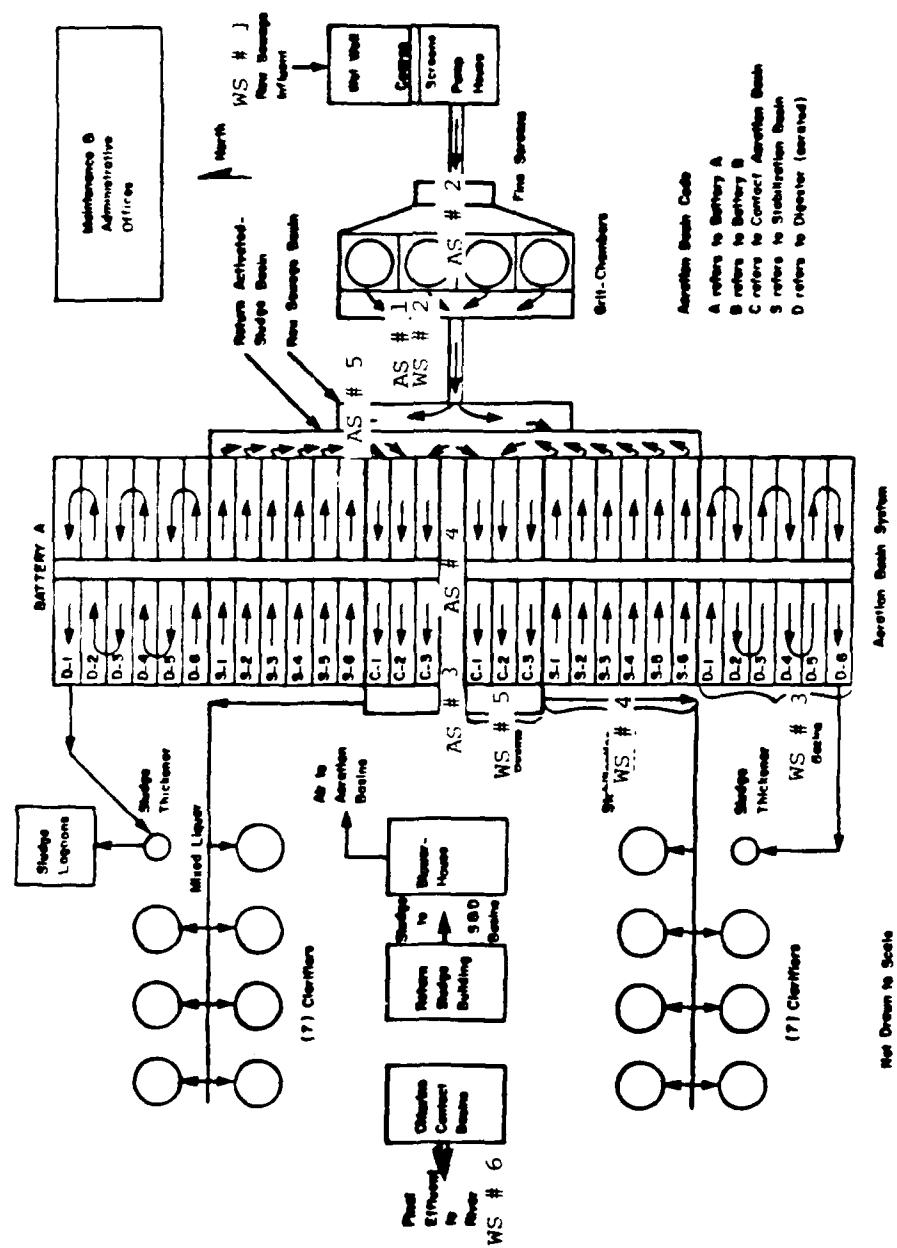
Figure 8.   Locations of Air and Wastewater
Sampling Positions for Clear
Night Survey (III)
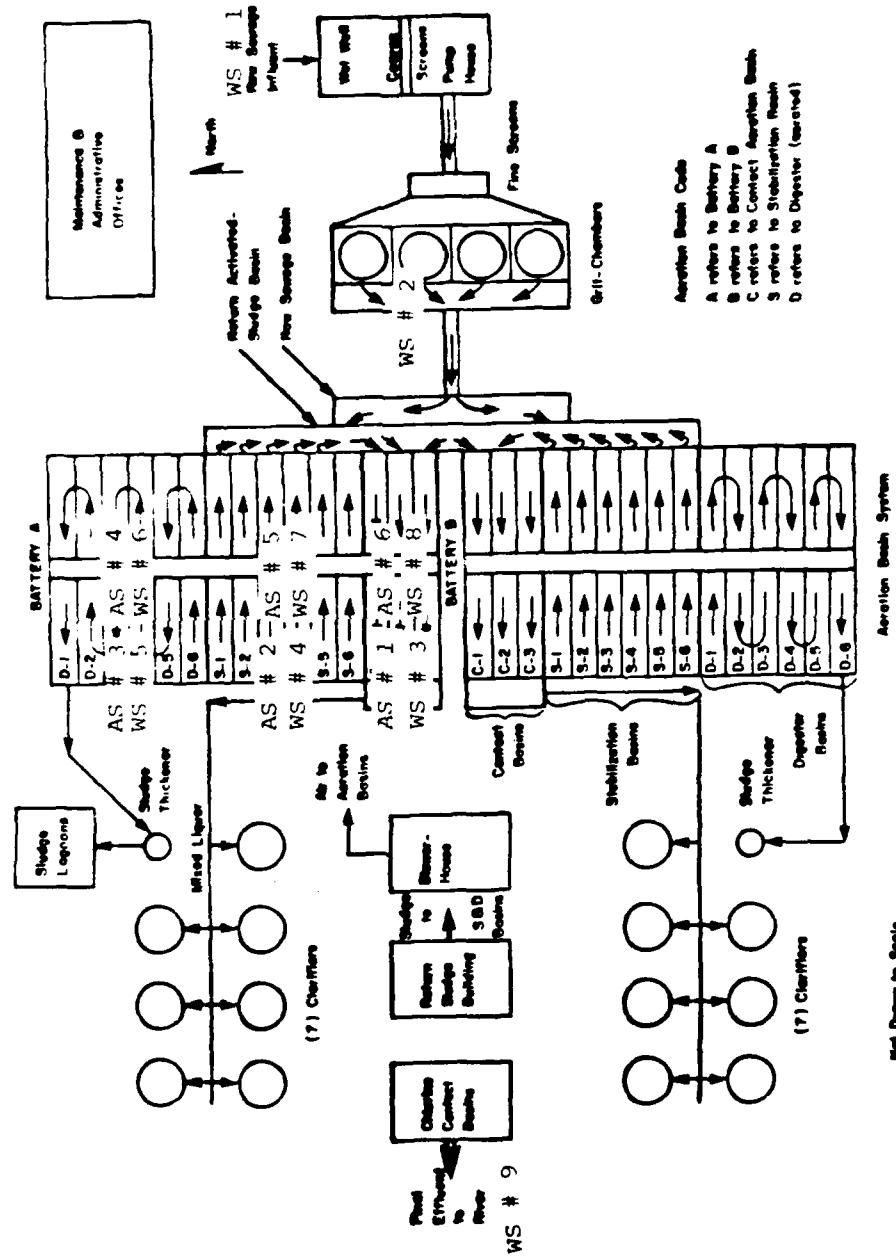
Figure 9.   Locations of Air and Wastewater
             Sampling Positions for Aeration
             Basins Survey (IV)
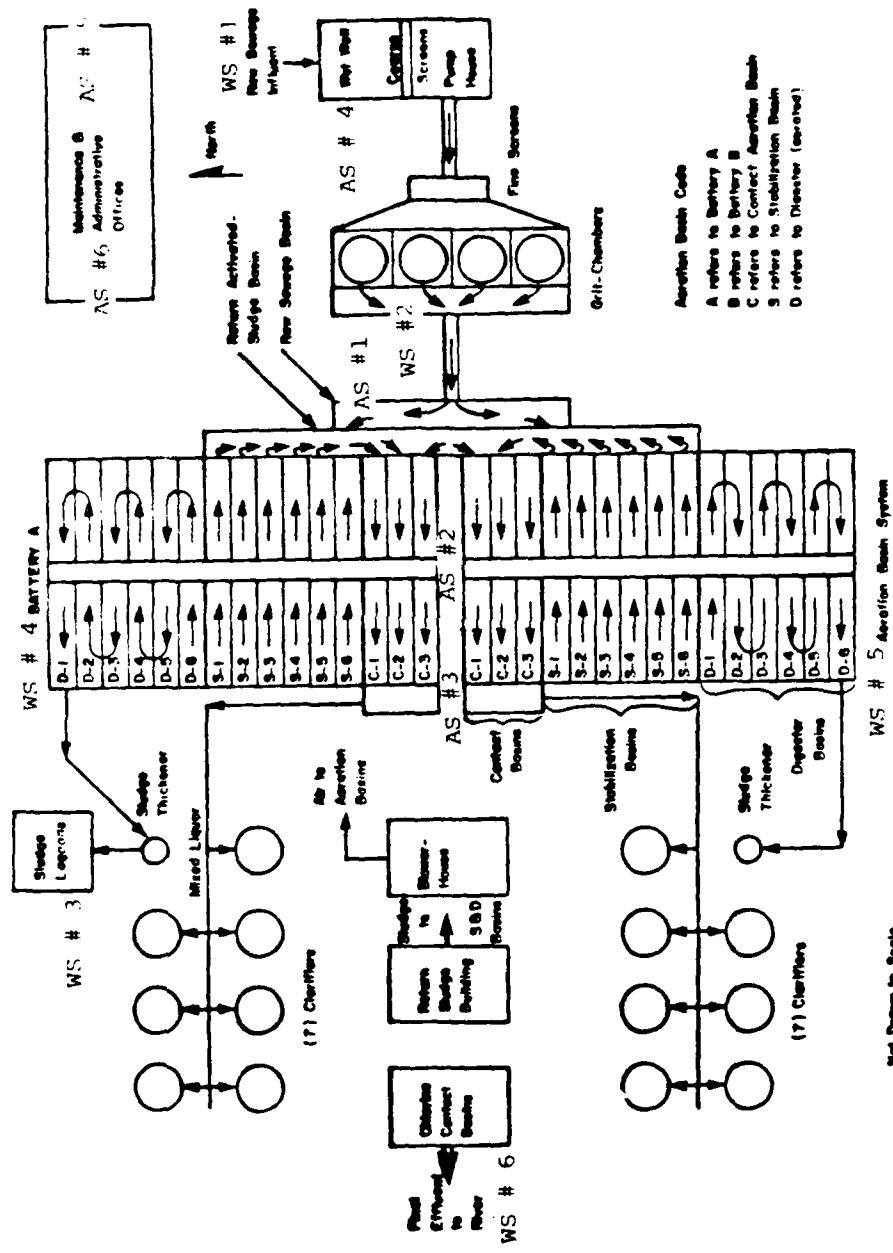
Figure 10. Locations of Air and Wastewater
Sampling Positions for Confined
Space Survey (V)

A# Air Sampling Position
W# Wastewater Sampling Position

A7 A9

W7 W9

Catwalk

A8A1ᴗ

W8

North

Catwalk

Wind from the West
1-2 MPH

Sludge Lagoon

A2
W2

A5
W5

A1
W1

Sludge Thickener

Mixed Liquor

A4
W4

A6
W6

A3
W3

North Double Row of Clarifiers
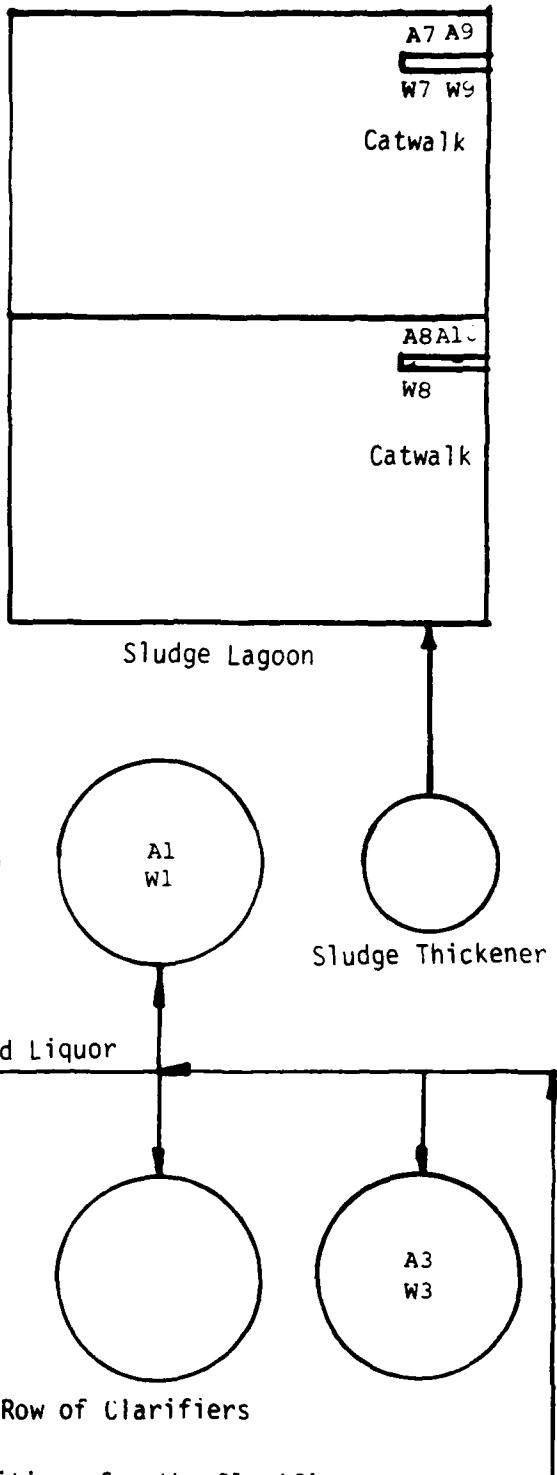
Figure 11.   Sampling Positions for the Clarifiers
and Lagoons Survey (VI)

A# Air Sampling Position
W# Wastewater Sampling Position

Contact Aeration Basins
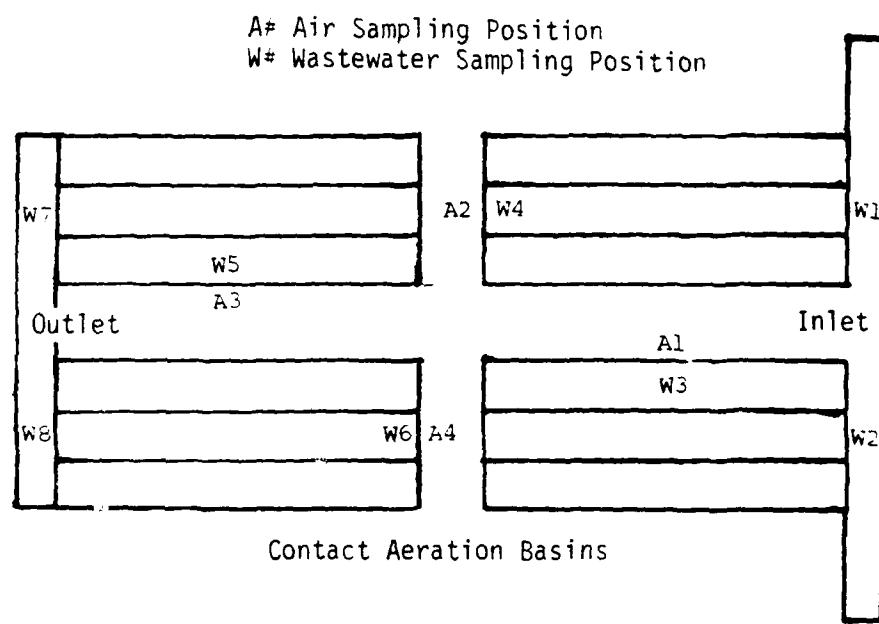
Figure 12. Sampling Positions for the Morning Contact
Aeration Basins Emission Rate Survey (VII)

A# Air Sampling Position
W# Wastewater Sampling Position

Contact Aeration Basins
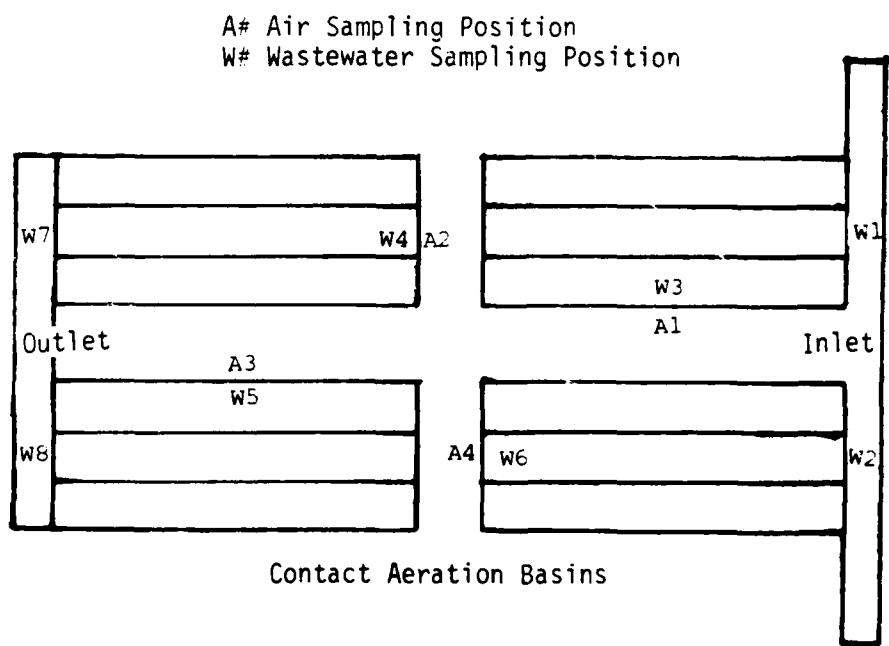
Figure 13. Sampling Positions for the Afternoon Contact
Aeration Basins Emission Rate Survey (VIII)
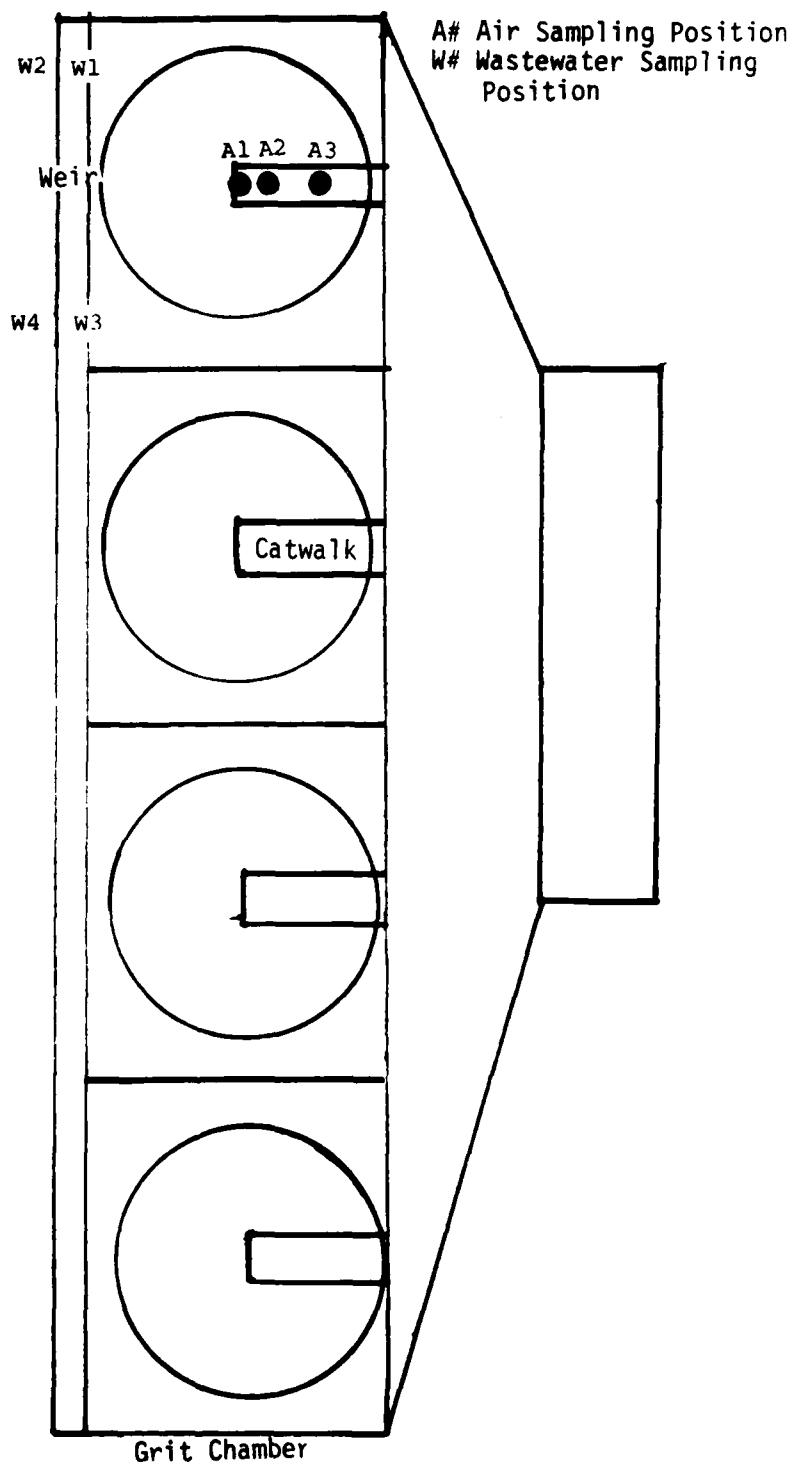
Figure 14. Sampling Positions of the Afternoon and
Morning Weir Emission Rate Surveys (IX and X)
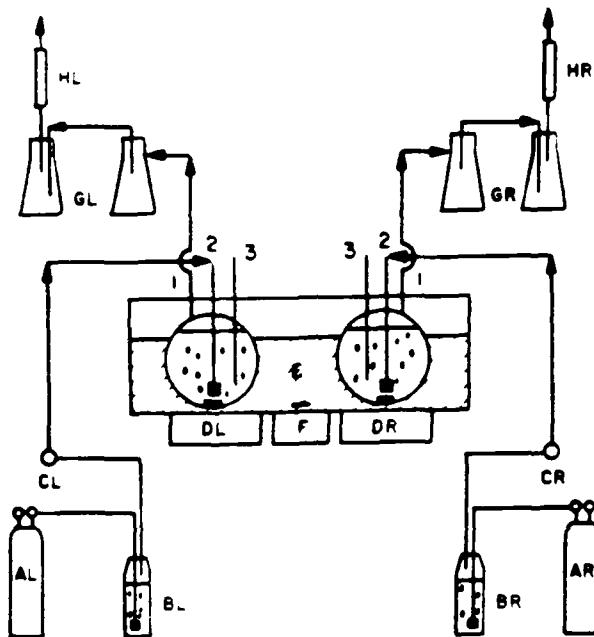
L refers to System #1
R refers to System #2

A Cylinder of Nitrogen
B Vapor Saturator of Water
C Fine Needle Control Valve
D Magnetic Stirrer with Rod in (2 liter) 3 Neck Round Bottom Flask
  1. Exit Stream Port
  2 Inlet Nitrogen Stream Port
  3. Wastewater Sampling Port
E Constant Temperature Water Bath
F Magnetic Stirrer with Rod in 10 Gal Water Tank
G Two (2) 500 ml Foam Traps
H Adsorbent Tube of Chromosorb 102

Figure 15.   Sketch of the Bench-Scale Aeration System
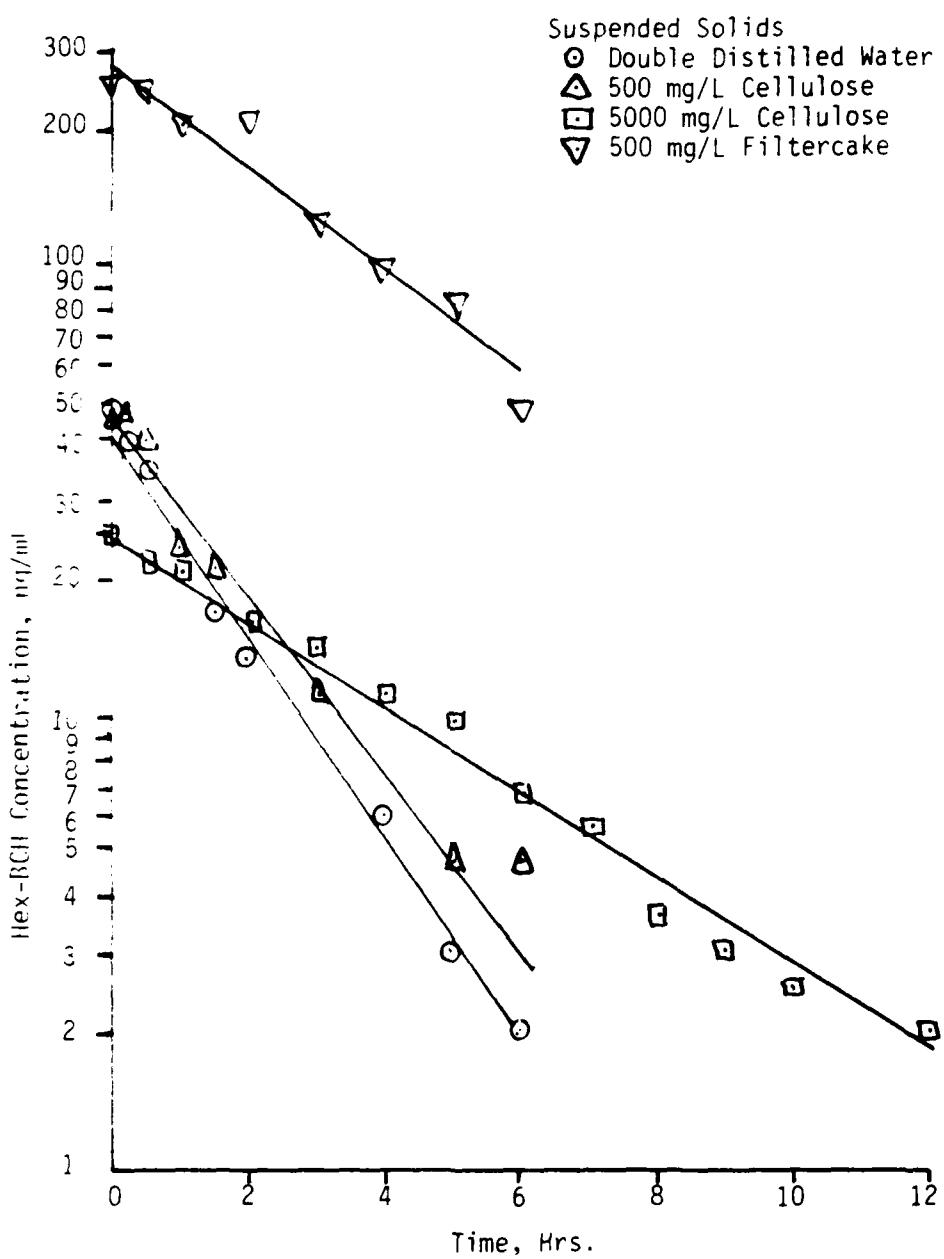
Figure 16. Results of the Initial Experiments
(Hex-BCH Wastewater Concentration
versus Time for Various Types of
Suspended Solids)
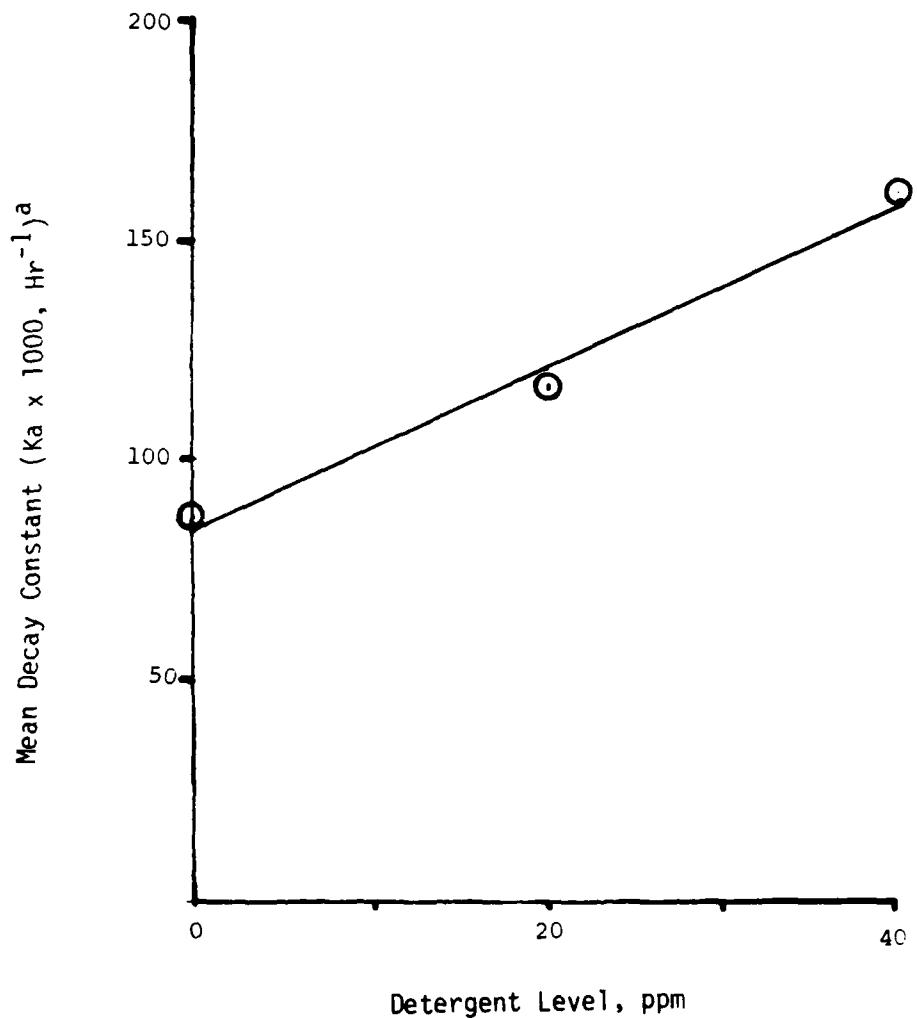
Figure 17. Mean Hex-BCH Decay Constant versus
            Detergent Level

a. The mean decay constant was the average of all (5x3x2)
experiments completed at each specific detergent level.

7.0 APPENDIX

7.1 Analytical Procedures

The air and wastewater analytical procedures for the Hex-related compounds was developed by Elia (34). The air analysis procedure was developed prior to the publication of the NIOSH method for Hex(35) (August 1979). The NIOSH method consists of drawing air through a Porapak T adsorbent tube, desorption with hexane, and analysis on a gas chromatograph with electron capture detector (GC/ECD). The next two sections will outline briefly the two procedures that were used in this study. Analysis for the chlorinated hydrocarbons (chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and tetrachloroethylene (TCE)) were done by the same method as described below for the Hex-related compounds. The identification of the Hex-BCH, Hex-VCL and chlordene peaks was established by comparison of sample retention times with a standard mix of these compounds. Spiking several samples with the standard mix did not generate isolated peaks or tailings on the peaks of the sample chromatograms, which suggests that these sample peaks represented Hex-BCH, Hex-VCL and chlordene. Additional confirmation was obtained on a second column (OV-17/QF1). The retention times of several samples of Hex-BCH, Hex-VCL and chlordene agreed within 0.1 minutes of the retention times of the standard mix.

7.1.1 Air Samples

The air sampler (MSA Model G pump or Bendix C115) pulled air at a constant flow rate through a glass sampling tube containing 100 mg of Chromosorb 102 (John Manville Corporation). The Chromosorb 102 is a

porous styrene-divinyl benzene copolmer solid sorbent, which has a high affinity for organic vapors. Unlike other sorbent materials such as charcoal, it will not adsorb water, which is a problem in sewage treatment environments. The organic compounds were extracted from the sorbent with 2 mL of petroleum ether (PE). After one hour, an aliquot of the desorbate was diluted 1 to 1000 and analysis completed with a 5 μl injection on an GC/ECD. Standard mixtures of the test compounds were used to calibrate the Hewlett-Packard 5830A GC, which provided electronic integration of the peak areas. The four feet long, 1/8 inch ID glass column contained 5% OV-101 liquid phase on Chromosorb GHP (80/100 mesh). Hex-related compound analysis was conducted at an oven temperature of 175°C and the more water-soluble compounds ($CHCl_3$, CCl_4, TCE) at 60°C.

The Chromosorb 102 (80/100 mesh) sorbent was initially purified by Soxhlet extraction for 4 hours each with methanol, acetone, and then petroleum ether (PE). The treated Chromosorb 102 was then tested on the GC/ECD to verify its purity. If the material was still impure, the Soxhlet extraction was repeated until purity could be obtained. The purified Chromosorb 102 was stored in a glass container away from the Hex-related standards and samples and retested prior to preparing the adsorbent tubes. The Chromosorb 102 was weighted (100 mg) and sealed in glass tubing with glass wool plugs. The ends were sealed with a propane/air torch. However, if the glass wool plugs were scorched during the sealing operation, the tube was rejected. Blank Chromosorb 102 tubes with scorched glass wool gave chromatograms with interfering peaks.

7.1.2 Wastewater Samples

Wastewater samples were 100 ml grab samples. The samples were collected in acid-rinsed, acetone-rinsed and sterilized 150 mL glass bottles with aluminum foil lined caps. The samples were transported from the field to the laboratory in a cooler at approximately $5^{o}C$. All laboratory wastewater samples were 5 mL aliquots.

Sample preparation of the wastewater samples began by saturation with sodium chloride of a 5 mL aliquot of the field samples or the 5 mL laboratory-study samples, followed by extraction with an equal amount of PE and shaking for 5 minutes. Analysis was completed by a 5 μl injection on the GC/ECD. If the analysis was not completed immediately after sample preparation, the PE extracts were stored in a freezer until time of analysis. In no case did the freezer storage time exceed more than three days. Even after a week, the Hex-related compounds (Hex-BCH, Hex-VCL and chlordene) were stable during freezer storage whereas chloroform had undergone decomposition.

Appendix 7.2
Program for

HP-55 Program Form

Calculation of the Decay Constant (Ka) & Correlation Coeff.(R)   1   1

DISPLAY		KEY	X	Y	Z	T	COMMENTS	REGISTERS
LINE	CODE	ENTER						R
	01	x/y					Model:	
	11	f					$Y = b_0 + b_1 X$	
	22	ln					Y = ln Concentration	
	22	x/y					X = Time (hr.)	
	41	+					Y = (ng/ml.	
	-21	go to D					PROCEDURE:	
	RL	stop					ENTER Conc. (ng/ml)	
	-21	go to D					in Y Register	
	33	store					ENTER TIME (hr.)	
	01	reg 0					in X Register	
	31	/					Press R/S	
	33	s					ENTER next CONC &	
	22	x/y					TIME VALUE, once	
	41	+					this is completed,	
	34	recall					PRESS f.L.R..X/Y	
	01	reg 0					READ Ka in X Reg.	
	71	*					PRESS GTO,0,9,R/S	
	-21	go to D					READ R in X Reg.	
	RL	stop						
	-21	go to D					NOTE: $R = S_x/S_y * b_1$	
								R.0
								R.1
								R.2
								R.3
								R.4
								R.5
								R.6
								R.7
								R.8
								R.9

Appendix 7-3   **HP-55 Program Form**

Aeration Rate Model Program

DISPLAY		KEY	X	Y	Z	T	COMMENTS	REGISTERS
LINE	CODE	ENTRY						R.
							Model:	
	31	f					$Ka = CQ^N$	
	22	ln					recall:	
	33	sto					ln axt=lna + lnt	
	00	0						
	22	x⇄y					$ln\ a^N = Nln\ a$	
	31	f					$ln\ Ka = lnCQ^N$	
	22	ln					$ln\ Ka = lnC+NlnC$	
	34	rcl					Linear Regression	
	00	0					Model:	
	11	+					$Y = lnKa$	
	-00	go to 0					$X = ln\ Q$	
	84	stop					Y-Intercept=lnC	
	-00	go to 3					Slope = N	
	33	sto						
	00	0					Procedure:	
	32	g					1. enter Ka into Y	
	33	sto					enter Q into X	
	22	x⇄y					Press R/S	
	81	÷					2. Repeat step 1	
	34	rcl					until all data is	
	00	0					entered.	
	71	x					3. Press f,L.R.	
	-00	go to 0					Read Y-Intercept in	
	84	stop					X register.	
	-00	go to 0					4. Press g, e^x and	
							read C in the x-reg.	
							5. Press x⇄y,read N	
							in the x-reg.	
							6. Press GTO,1,4,R/S	
							7. Read Correlation	
							Coeff.,R in x-reg.	

REGISTERS column:
R.
R.
R.
R.
R.
R.
R.2
R.3
R.4
R.5
R.6
R.7
R.t
R.
R.8
R.9

Appendix 7.4 Weir Emission Rate Calculation for Hex-BCH

References: Section 1.2.6.2

Table 28

Figures 2, 3 and 14.

Summary of Calculations:

Sample #	Conc. ng/L	X m	σ_y m	σ_z m	P_1	P_2	$\frac{\int P_2}{P_1}$	W_d g/min
1.	2.692	8.92	3.03	1.42	+2.61	-2.61	0.991	0.016
2.	1.586	10.0	3.36	1.58	+2.36	-2.36	0.965	0.011
3.	1.193	15.0	4.85	2.32	+1.63	-1.63	0.908	0.012

Avg. W_d = 0.013 g/min

S = 0.003 g/min

The weather was fair with approximately 20% cloud coverage and a wind velocity of less than two mps. This would imply greater than 60° solar altitude (37), which Turner classified as an A Stability Class (25). The σ_y and σ_z values were determined by the Zimmerman and Thompson method (38) since the workbook on atmospheric dispersion by Turner (25) did not report σ_y and σ_z values for short downwind distances.

$$\sigma_y = 465.1(X + b)\tan\theta_p$$

where σ_y = crosswind dispersion parameter, m.

X = downwind distance from the line source to receptor,m.

b = virtual distance, Km (assume b = 0).

θ_p = half-angle of hortizontal plume spreading, where

$\theta_p = c - d\ln(X - b/X_0)$

c = 24.17 for Stability Class A

$$d = 2.53 \text{ for Stability Class A}$$

therefore,

$$\sigma_y = 465.1(X/1000)\tan(24.17 - 2.53\ln(X/1000)$$

$$\sigma_z = \frac{g(X + a)^h}{X}$$

where σ_z = altitude dispersion parameter, m.

a = virtual distance (assume $a = 0$).

X_0= 1 Km.

g = 122.8 for Stability Class A

h = 0.99 for Stability Class A

therefore,

$$\sigma_z = 122.8(X/1000)^{0.99}$$

Martin (26) specified that air sampling for over ten minutes required correction of the concentration value to an estimated three to ten minute concentration value to utilize the atmospheric dispersion model equation (Eq. 17). Since the air sampling survey was for 30 minutes, the Martin procedure was carried out as follows:

$$C_0 = C/(T_0/T)^P$$

where C_0 = corrected ten minute concentration value, ng/L.

C = 30 minute reported concentration value, ng/L.

T_0 = corrected concentreation time of ten minutes.

T ≠ actual survey time of 30 minutes.

P = correction factor, which is a function of Stability Class (For Stability Class A, P = 0.36).

therefore,

$$C_o = C/(10/30)^{0.36} = C/0.67 = 1.49 \ C$$

The $\int_{P_1}^{P_2} 1/\sqrt{2\pi} \exp(0.5P^2)dP$ term in the W_d equation (Eq. 17) was evaluated from standard statistical tables (25).

Appendix 7.5 Summary of Results of the Bench-Scale Aeration Unit

Appendix 7.5.1 Summary of Results at the 0 ppm Detergent Level

Flow Rate $\frac{cc}{min}$	SS Conc $\frac{mg}{L}$	Hex-BCH System # 1 Ka	R	Hex-BCH System # 2 Ka	R	Chloroform System # 1 Ka	R	Chloroform System # 2 Ka	R
17.5	500	-0.021	-0.999	-0.035	-0.863	-0.105	-0.998	-0.078	-0.967
17.5	1000	-0.018	-0.787	-0.021	-0.915	-0.087	-0.997	-0.072	-0.995
17.5	1500	-0.032	-0.784	-0.039	-0.903	-0.088	-0.989	-0.077	-0.990
35	500	-0.066	-0.925	-0.080	-0.818	-0.155	-0.995	-0.150	-0.994
35	1000	-0.059	-0.887	-0.083	-0.901	-0.223	-0.919	-0.199	-0.977
35	1500	-0.036	-0.614	-0.048	-0.992	-0.149	-0.990	-0.193	-0.997
70	500	-0.102	-0.971	-0.108	-0.880	-0.333	-0.998	-0.249	-0.999
70	1000	-0.051	-0.874	-0.038	-0.714	-0.280	-0.997	-0.326	-0.999
70	1500	-0.034	-0.976	-0.041	-0.962	-0.324	-0.999	-0.311	-0.998
140	500	-0.125	-0.993	-0.175	-0.996	-0.588	-0.999	-0.670	-0.999
140	1000	-0.077	-0.945	-0.057	-0.981	-0.596	-0.999	-0.624	-0.999
140	1500	-0.035	-0.722	-0.057	-0.927	-0.544	-0.999	-0.631	-0.999
280	500	-0.239	-0.980	-0.272	-0.998	-1.169	-0.990	-1.088	-0.993
280	1000	-0.146	-0.993	-0.163	-0.998	-0.932	-0.995	-1.107	-0.993
280	1500	-0.117	-0.950	-0.207	-0.906	-0.930	-0.992	-0.746	-0.980
35	0.0	-0.112	-0.957	------	------	-0.152	-0.990	------	-------

Appendix 7.5.2 Summary of Results at the 20 ppm Detergent Level

Flow Rate cc/min	SS Conc mg/L	Hex-BCH System # 1		System # 2		Chloroform System # 1		System # 2	
		Ka	R	Ka	R	Ka	R	Ka	R
17.5	500	-0.102	-0.952	-0.082	-0.984	-0.073	-0.979	-0.111	-0.988
17.5	1000	-0.062	-0.969	-0.088	-0.986	-0.069	-0.981	-0.123	-0.992
17.5	1500	-0.059	-0.845	-0.068	-0.952	-0.056	-0.906	-0.081	-0.993
35	500	-0.083	-0.954	-0.077	-0.965	-0.158	-0.997	-0.137	-0.992
35	1000	-0.079	-0.989	-0.055	-0.980	-0.180	-0.994	-0.141	-0.999
35	1500	-0.023	-0.796	-0.022	-0.902	-0.168	-0.997	-0.156	-0.995
70	500	-0.099	-0.955	-0.099	-0.957	-0.287	-0.999	-0.297	-0.997
70	1000	-0.103	-0.883	-0.074	-0.846	-0.381	-0.996	-0.375	-0.998
70	1500	-0.036	-0.826	-0.051	-0.947	-0.308	-0.999	-0.298	-0.998
140	500	-0.223	-0.983	-0.243	-0.992	-0.602	-0.996	-0.595	-0.993
140	1000	-0.159	-0.976	-0.128	-0.987	-0.567	-0.999	-0.610	-0.999
140	1500	-0.095	-0.985	-0.103	-0.940	-0.535	-0.999	-0.650	-0.996
280	500	-0.252	-0.961	-0.274	-0.984	-1.066	-0.997	-0.984	-0.999
280	1000	-0.212	-0.981	-0.228	-0.997	-1.000	-0.999	-1.043	-0.997
280	1500	-0.175	-0.999	-0.203	-0.998	-0.961	-0.998	-0.926	-0.986

Appendix 7.5.3 Summary of Results at the 40 ppm Detergent Level

Flow Rate $\frac{cc}{min}$	SS Conc $\frac{mg}{L}$	Hex-BCH				Chloroform			
		System # 1		System # 2		System # 1		System # 2	
		Ka	R	Ka	R	Ka	R	Ka	R
17.5	500	-0.031	-0.937	-0.029	-0.888	-0.069	-0.992	-0.065	-0.941
17.5	1000	-0.046	-0.958	-0.056	-0.985	-0.088	-0.971	-0.087	-0.994
17.5	1500	-0.008	-0.888	-0.027	-0.872	-0.068	-0.976	-0.083	-0.962
35	500	-0.141	-0.861	-0.088	-0.943	-0.271	-0.951	-0.152	-0.998
35	1000	-0.065	-0.929	-0.095	-0.927	-0.160	-0.995	-0.223	-0.999
35	1500	-0.039	-0.963	-0.031	-0.916	-0.191	-0.989	-0.162	-0.995
70	500	-0.138	-0.989	-0.159	-0.987	-0.281	-0.995	-0.319	-0.997
70	1000	-0.090	-0.973	-0.138	-0.960	-0.275	-0.991	-0.291	-0.998
70	1500	-0.046	-0.988	-0.080	-0.971	-0.337	-0.999	-0.282	-0.999
140	500	-0.286	-0.975	-0.314	-0.962	-0.580	-0.999	-0.560	-0.999
140	1000	-0.156	-0.930	-0.201	-0.931	-0.545	-0.999	-0.560	-0.999
140	1500	-0.163	-0.858	-0.144	-0.831	-0.561	-0.990	-0.563	-0.990
280	500	-0.485	-0.987	-0.456	-0.971	-1.128	-0.995	-1.045	-0.998
280	1000	-0.336	-0.992	-0.363	-0.972	-1.115	-0.995	-1.072	-0.998
280	1500	-0.200	-0.950	-0.262	-0.977	-0.997	-0.999	-1.082	-0.998

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